Hydration induced protomer switching in *p*-aminobenzoic acid studied by cold ion trap infrared spectroscopy

Supplementary Material

Table of Content

Table S1 Gibbs free energy (80K) of conformers of $PABAH^+$.

Conf.	ΔG / kJ mol^{-1}
O-0-1	0
O-0-2	12.9
O-0-3	22.9
N-0-1	24.1
N-0-2	68.0

Table S2 Gibbs free energy (80 K) of conformers of $PABAH^+(H_2O)$.

Conf.	ΔG / kJ mol^{-1}
O-1-1	0.0
O-1-2	4.3
O-1-3	5.0
N-1-1	23.4
N-1-2	23.5
O-1-4	25.5
O-1-5	31.2
O-1-6	31.3
O-1-7	46.9
N-1-3	50.6
C-1-1	51.9
O-1-8	52.6
C-1-2	52.9
C-1-3	53.6
C-1-4	55.6
C-1-5	58.0
C-1-6	60.2
N-1-4	65.1
N-1-5	65.1
N-1-6	92.3

Table S3 Gibbs free energy (80 K) of conformers of $PABAH^+(H_2O)_2$.

Conf.	ΔG / kJ mol^{-1}
O-2-1	0.0
O-2-2	0.1
O-2-3	1.2

O-2-4	**1.2**
O-2-5	**11.4**
O-2-6	**11.4**
O-2-7	**15.2**
O-2-8	**15.5**
N-2-1	**17.3**
N-2-2	**17.9**
O-2-9	**19.8**
O-2-10	**20.0**
O-2-11	**20.0**
O-2-12	**20.0**
O-2-13	**20.0**
O-2-14	**24.0**
O-2-15	**24.4**
O-2-16	**24.4**
O-2-17	**24.7**
N-2-3	**29.8**
N-2-4	**29.8**
N-2-5	**30.3**
N-2-6	**30.3**
N-2-7	**30.6**
N-2-8	**30.6**
O-2-18	**31.9**
O-2-19	**33.8**
N-2-9	**35.5**
N-2-10	**35.5**
N-2-11	**35.5**
O-2-20	**44.1**
O-2-21	**44.4**
O-2-22	**51.2**
O-2-23	**51.2**
O-2-24	**52.1**
O-2-25	**52.1**
O-2-26	**52.1**
O-2-27	**52.1**
N-2-12	**58.4**
N-2-13	**59.1**

N-2-14	**60.1**
O-2-28	**67.7**
O-2-29	**68.1**
O-2-30	**68.2**
N-2-15	**70.3**
N-2-16	**70.3**
N-2-17	**70.6**
N-2-18	**70.6**
N-2-19	**70.9**
N-2-20	**71.7**
O-2-31	**71.9**
O-2-32	**72.7**
O-2-33	**72.8**
N-2-21	**75.9**
N-2-22	**75.9**

Table S4 Gibbs free energy (80 K) of conformers of $PABAH^+(H_2O)_3$.

Conf.	ΔG / kJ mol^{-1}
O-3-1	**0**
O-3-2	**0**
O-3-3	**0**
O-3-4	**0.3**
O-3-5	**0.3**
O-3-6	**0.6**
O-3-7	**2.0**
O-3-8	**2.0**
O-3-9	**2.1**
O-3-10	**2.1**
O-3-11	**2.1**
O-3-12	**3.9**
O-3-13	**3.9**
O-3-14	**3.9**
O-3-15	**6.6**
O-3-16	**6.6**
O-3-17	**6.6**
O-3-18	**6.7**
O-3-19	**6.7**

O-3-20	**6.7**
O-3-21	**6.7**
N-3-1	**10.5**
O-3-22	**13.0**
O-3-23	**13.0**
O-3-24	**13.0**
O-3-25	**13.0**
O-3-26	**13.0**
N-3-2	**17.8**
N-3-3	**17.8**
N-3-4	**17.8**
O-3-27	**18.6**
O-3-28	**18.6**
O-3-29	**18.6**
O-3-30	**18.6**
N-3-5	**18.7**
N-3-6	**18.7**
N-3-7	**18.8**
N-3-8	**18.8**
N-3-9	**19.7**
N-3-10	**19.7**
N-3-11	**19.7**
N-3-12	**19.7**
N-3-13	**19.7**
N-3-14	**19.7**
N-3-15	**19.7**
N-3-16	**19.7**
N-3-17	**19.7**
N-3-18	**19.7**
N-3-19	**19.7**
N-3-20	**19.7**
N-3-21	**19.7**
N-3-22	**19.7**
N-3-23	**19.7**
N-3-24	**19.8**
N-3-25	**20.4**
N-3-26	**20.4**

N-3-27	**20.4**
N-3-28	**20.4**

Table S5 Gibbs free energy (80 K) of conformers of $PABAH^+(H_2O)_4$.

Conf.	**ΔG / kJ mol^{-1}**
O-4-1	**0.0**
O-4-2	**0.0**
O-4-3	**0.0**
O-4-4	**0.0**
O-4-5	**0.6**
O-4-6	**0.6**
O-4-7	**0.6**
O-4-8	**0.6**
O-4-9	**0.6**
O-4-10	**1.3**
O-4-11	**1.3**
O-4-12	**4.2**
O-4-13	**4.2**
O-4-14	**4.2**
O-4-15	**4.6**
O-4-16	**4.6**
O-4-17	**4.9**
O-4-18	**4.9**
O-4-19	**4.9**
O-4-20	**4.9**
O-4-21	**4.9**
O-4-22	**4.9**
O-4-23	**4.9**
O-4-24	**4.9**
O-4-25	**4.9**
O-4-26	**4.9**
O-4-27	**4.9**
O-4-28	**4.9**
O-4-29	**5.0**
O-4-30	**5.8**
O-4-31	**5.9**
O-4-32	**6.4**

O-4-33	**6.4**
O-4-34	**6.4**
O-4-35	**6.4**
O-4-36	**6.4**
O-4-37	**6.4**
O-4-38	**6.4**
O-4-39	**7.8**
O-4-40	**7.8**
O-4-41	**8.0**
O-4-42	**8.0**
O-4-43	**8.0**
O-4-44	**8.0**
O-4-45	**8.0**
O-4-46	**8.0**
O-4-47	**8.0**
O-4-48	**9.7**
O-4-49	**9.7**
O-4-50	**9.7**
O-4-51	**9.7**
O-4-52	**9.7**
O-4-53	**9.7**
O-4-54	**10.1**
O-4-55	**10.1**
O-4-56	**10.1**
O-4-57	**10.1**
O-4-58	**10.1**
O-4-59	**10.1**
O-4-60	**10.1**
O-4-61	**10.2**
O-4-62	**10.5**
O-4-63	**10.5**
O-4-64	**10.5**
O-4-65	**11.7**
O-4-66	**11.8**
O-4-67	**11.8**
O-4-68	**12.0**
O-4-69	**12.0**

O-4-70	**12.0**
O-4-71	**12.0**
N-4-1	**12.1**
N-4-2	**12.2**
N-4-3	**12.3**
N-4-4	**12.4**
O-4-72	**12.5**
N-4-5	**12.6**
N-4-6	**12.6**
O-4-73	**13.1**
O-4-74	**13.2**
N-4-7	**13.5**
N-4-8	**13.5**
N-4-9	**13.5**
N-4-10	**13.5**
N-4-11	**13.5**
N-4-12	**14.0**
N-4-13	**14.0**
N-4-14	**14.0**
N-4-15	**14.0**
N-4-16	**14.0**
N-4-17	**14.0**
O-4-75	**14.3**
O-4-76	**14.3**
O-4-77	**14.3**
O-4-78	**14.3**
N-4-18	**14.4**
N-4-19	**14.4**
N-4-20	**14.4**
O-4-79	**15.9**
O-4-80	**15.9**
N-4-21	**16.3**
O-4-81	**16.5**
O-4-82	**16.5**
O-4-83	**16.5**
O-4-84	**16.5**
N-4-22	**16.7**

N-4-23	**16.7**
N-4-24	**17.1**
N-4-25	**17.2**
N-4-26	**17.2**
O-4-85	**18.6**
O-4-86	**18.6**
N-4-27	**19.8**
N-4-28	**20.5**
N-4-29	**20.5**
N-4-30	**20.5**
N-4-31	**20.5**
N-4-32	**20.6**
N-4-33	**20.6**
N-4-34	**20.6**
N-4-35	**20.6**
N-4-36	**20.6**
N-4-37	**20.7**
N-4-38	**20.7**
N-4-39	**20.8**
N-4-40	**20.8**
N-4-41	**20.8**
N-4-42	**20.8**
N-4-43	**20.8**
N-4-44	**21.1**
N-4-45	**21.1**
N-4-46	**21.1**
N-4-47	**21.1**
N-4-48	**21.1**
N-4-49	**21.1**
N-4-50	**21.1**
N-4-51	**21.1**
N-4-52	**21.1**
N-4-53	**21.2**
N-4-54	**21.2**
N-4-55	**21.2**
N-4-56	**21.3**
N-4-57	**21.7**

N-4-58	**21.7**
N-4-59	**21.8**
N-4-60	**22.3**
N-4-61	**22.3**
N-4-62	**23.2**
N-4-63	**23.2**

Table S6 Gibbs free energy (80 K) of conformers of $PABAH^+(H_2O)_5$.

Conf.	**ΔG / kJ mol^{-1}**
O-5-1	**0.0**
O-5-2	**0.2**
O-5-3	**0.3**
O-5-4	**1.2**
O-5-5	**1.2**
O-5-6	**2.0**
O-5-7	**2.0**
O-5-8	**2.4**
O-5-9	**2.4**
O-5-10	**2.4**
O-5-11	**3.2**
O-5-12	**3.2**
O-5-13	**3.2**
O-5-14	**3.2**
O-5-15	**3.3**
O-5-16	**3.3**
O-5-17	**3.3**
O-5-18	**3.5**
N-5-1	**3.5**
N-5-2	**3.5**
N-5-3	**3.5**
O-5-19	**3.9**
O-5-20	**3.9**
O-5-21	**4.5**
O-5-22	**4.7**
O-5-23	**4.8**
N-5-4	**5.3**
N-5-5	**5.3**

O-5-24	**5.7**
O-5-25	**5.8**
O-5-26	**5.9**
O-5-27	**5.9**
O-5-28	**5.9**
O-5-29	**6.0**
O-5-30	**6.8**
N-5-6	**6.9**
N-5-7	**7.1**
O-5-31	**7.2**
O-5-32	**7.5**
O-5-33	**7.7**
O-5-34	**8.1**
O-5-35	**8.2**
O-5-36	**8.2**
O-5-37	**8.2**
O-5-38	**8.2**
O-5-39	**8.4**
O-5-40	**8.4**
N-5-8	**8.7**
N-5-9	**8.7**
O-5-41	**8.7**
O-5-42	**8.7**
N-5-10	**8.8**
N-5-11	**8.9**
N-5-12	**9.0**
N-5-13	**9.0**
O-5-43	**9.0**
O-5-44	**9.1**
N-5-14	**9.1**
O-5-45	**9.7**
O-5-46	**9.7**
O-5-47	**9.8**
O-5-48	**9.8**
O-5-49	**9.8**
O-5-50	**9.8**
O-5-51	**9.9**

O-5-52	**10.0**
O-5-53	**10.0**
O-5-54	**10.8**
N-5-15	**11.1**
O-5-55	**11.2**
O-5-56	**11.2**
O-5-57	**11.2**
O-5-58	**11.5**
N-5-16	**11.7**
N-5-17	**11.7**
N-5-18	**12.1**
N-5-19	**12.1**
N-5-20	**12.1**
N-5-21	**12.1**
O-5-59	**12.4**
O-5-60	**12.4**
N-5-22	**12.4**
N-5-23	**12.6**
N-5-24	**12.6**
N-5-25	**12.6**
N-5-26	**12.7**
N-5-27	**12.7**
N-5-28	**12.7**
N-5-29	**12.7**
N-5-30	**12.8**
N-5-31	**12.8**
N-5-32	**12.8**
O-5-61	**12.8**
O-5-62	**12.8**
O-5-63	**12.9**
O-5-64	**12.9**
O-5-65	**12.9**
N-5-33	**13.1**
N-5-34	**13.1**
N-5-35	**13.1**
O-5-66	**13.1**
O-5-67	**13.1**

O-5-68	**13.1**
O-5-69	**13.2**
O-5-70	**13.2**
O-5-71	**13.4**
O-5-72	**13.5**
N-5-36	**13.5**
N-5-37	**13.6**
N-5-38	**13.6**
N-5-39	**13.6**
N-5-40	**13.7**
N-5-41	**13.8**
N-5-42	**13.8**
N-5-43	**13.8**
N-5-44	**13.8**
N-5-45	**13.8**
N-5-46	**14.0**
N-5-47	**14.1**
N-5-48	**14.1**
N-5-49	**14.2**
N-5-50	**14.3**
N-5-51	**14.3**
N-5-52	**14.4**
N-5-53	**14.4**
N-5-54	**14.5**
N-5-55	**14.6**
O-5-73	**14.7**
N-5-56	**14.9**
N-5-57	**14.9**
O-5-74	**15.0**
O-5-75	**15.0**
N-5-58	**15.1**
N-5-59	**15.2**
N-5-60	**15.2**
N-5-61	**15.2**
O-5-76	**15.3**
N-5-62	**15.4**
O-5-77	**15.5**

O-5-78	**15.5**
N-5-63	**15.6**
N-5-64	**15.6**
O-5-79	**15.6**
O-5-80	**15.6**
N-5-65	**15.7**
N-5-66	**16.1**
N-5-67	**16.1**
N-5-68	**16.2**
N-5-69	**16.7**
N-5-70	**16.7**
N-5-71	**16.7**
N-5-72	**16.7**
N-5-73	**16.7**
N-5-74	**16.7**
O-5-81	**17.2**
O-5-82	**17.2**
N-5-75	**17.3**
N-5-76	**17.4**
O-5-83	**17.5**
N-5-77	**17.6**
N-5-78	**17.6**
N-5-79	**17.7**
N-5-80	**17.9**
N-5-81	**17.9**
N-5-82	**18.1**
N-5-83	**18.1**
N-5-84	**18.1**
N-5-85	**18.1**
N-5-86	**18.1**
N-5-87	**18.3**
N-5-88	**18.3**
N-5-89	**18.3**
N-5-90	**18.3**
N-5-91	**18.3**
N-5-92	**18.3**
N-5-93	**18.3**

O-5-84	**18.7**
O-5-85	**18.7**
N-5-94	**19.0**
N-5-95	**19.3**
N-5-96	**19.3**
N-5-97	**19.3**
O-5-86	**19.6**
N-5-98	**19.7**
N-5-99	**19.9**
N-5-100	**19.9**
N-5-101	**19.9**
N-5-102	**20.0**
N-5-103	**20.3**
N-5-104	**20.5**
N-5-105	**20.8**
N-5-106	**20.9**
N-5-107	**21.3**
N-5-108	**21.3**
N-5-109	**27.1**

Table S7 Gibbs free energy (80 K) of conformers of $PABAH^+(H_2O)_6$.

Conf.	**ΔG / kJ mol^{-1}**
N-6-1	**0.0**
N-6-2	**0.1**
N-6-3	**0.2**
O-6-1	**1.4**
O-6-2	**1.5**
O-6-3	**2.1**
O-6-4	**2.2**
O-6-5	**2.2**
O-6-6	**2.2**
O-6-7	**2.2**
O-6-8	**2.4**
O-6-9	**2.6**
O-6-10	**2.8**
O-6-11	**2.9**
O-6-12	**3.0**

O-6-13	**3.6**
O-6-14	**3.6**
O-6-15	**3.6**
O-6-16	**3.7**
O-6-17	**3.7**
O-6-18	**3.8**
O-6-19	**3.8**
O-6-20	**3.8**
O-6-21	**5.0**
O-6-22	**5.0**
O-6-23	**5.0**
O-6-24	**5.0**
O-6-25	**5.0**
O-6-26	**5.2**
O-6-27	**5.2**
O-6-28	**5.7**
N-6-4	**6.0**
N-6-5	**6.0**
O-6-29	**6.1**
O-6-30	**6.2**
O-6-31	**6.3**
O-6-32	**6.3**
O-6-33	**6.4**
O-6-34	**6.4**
O-6-35	**6.6**
O-6-36	**6.7**
O-6-37	**6.7**
O-6-38	**6.8**
O-6-39	**6.9**
O-6-40	**6.9**
O-6-41	**6.9**
O-6-42	**6.9**
N-6-6	**6.9**
O-6-43	**7.0**
O-6-44	**7.0**
O-6-45	**7.0**
O-6-46	**7.0**

N-6-7	**7.2**
N-6-8	**7.2**
N-6-9	**7.2**
O-6-47	**7.4**
O-6-48	**7.4**
N-6-10	**7.5**
O-6-49	**7.6**
N-6-11	**7.7**
O-6-50	**7.7**
O-6-51	**7.7**
O-6-52	**7.9**
O-6-53	**7.9**
O-6-54	**8.0**
O-6-55	**8.1**
O-6-56	**8.3**
O-6-57	**8.4**
O-6-58	**8.5**
O-6-59	**8.9**
O-6-60	**8.9**
O-6-61	**8.9**
O-6-62	**8.9**
O-6-63	**9.1**
O-6-64	**9.1**
O-6-65	**9.1**
O-6-66	**9.1**
O-6-67	**9.1**
O-6-68	**9.1**
O-6-69	**9.2**
O-6-70	**9.2**
N-6-12	**9.2**
N-6-13	**9.2**
O-6-71	**9.3**
O-6-72	**9.3**
O-6-73	**9.3**
O-6-74	**9.4**
O-6-75	**9.4**
O-6-76	**9.4**

O-6-77	**9.4**
O-6-78	**9.5**
O-6-79	**9.5**
O-6-80	**9.5**
O-6-81	**9.5**
O-6-82	**9.5**
O-6-83	**9.6**
O-6-84	**9.6**
O-6-85	**9.6**
N-6-14	**9.6**
N-6-15	**9.6**
O-6-86	**9.8**
O-6-87	**10.0**
N-6-16	**10.2**
N-6-17	**10.2**
N-6-18	**10.2**
O-6-88	**10.7**
O-6-89	**10.8**
O-6-90	**10.9**
O-6-91	**11.2**
O-6-92	**11.2**
O-6-93	**11.3**
O-6-94	**11.4**
O-6-95	**11.7**
O-6-96	**11.7**
O-6-97	**11.8**
O-6-98	**11.8**
O-6-99	**11.8**
O-6-100	**11.8**
N-6-19	**11.8**
N-6-20	**11.8**
N-6-21	**11.9**
O-6-101	**11.9**
O-6-102	**11.9**
O-6-103	**12.0**
O-6-104	**12.0**
O-6-105	**12.0**

N-6-22	**12.2**
N-6-23	**12.2**
N-6-24	**12.3**
O-6-106	**12.4**
N-6-25	**12.5**
N-6-26	**12.7**
N-6-27	**12.7**
N-6-28	**12.7**
N-6-29	**12.8**
N-6-30	**12.8**
N-6-31	**12.9**
O-6-107	**12.9**
O-6-108	**13.0**
N-6-32	**13.0**
N-6-33	**13.1**
N-6-34	**13.2**
N-6-35	**13.2**
O-6-109	**13.6**
N-6-36	**13.6**
N-6-37	**13.6**
N-6-38	**13.6**
N-6-39	**13.6**
N-6-40	**13.7**
N-6-41	**13.8**
O-6-110	**13.8**
O-6-111	**13.9**
O-6-112	**13.9**
O-6-113	**13.9**
N-6-42	**14.0**
O-6-114	**14.1**
O-6-115	**14.1**
N-6-43	**14.2**
O-6-116	**14.3**
N-6-44	**14.4**
N-6-45	**14.5**
N-6-46	**14.5**
N-6-47	**14.5**

N-6-48	**14.7**
N-6-49	**14.7**
N-6-50	**14.8**
O-6-117	**14.9**
N-6-51	**14.9**
N-6-52	**14.9**
O-6-118	**15.0**
N-6-53	**15.0**
N-6-54	**15.1**
N-6-55	**15.2**
N-6-56	**15.2**
N-6-57	**15.2**
N-6-58	**15.3**
N-6-59	**15.3**
N-6-60	**15.4**
N-6-61	**15.4**
N-6-62	**15.5**
N-6-63	**15.5**
N-6-64	**15.5**
N-6-65	**15.6**
N-6-66	**15.6**
N-6-67	**15.6**
N-6-68	**15.7**
N-6-69	**15.9**
N-6-70	**15.9**
N-6-71	**16.2**
N-6-72	**16.3**
N-6-73	**16.3**
N-6-74	**16.4**
N-6-75	**16.5**
N-6-76	**16.7**
N-6-77	**16.7**
N-6-78	**16.8**
O-6-119	**16.8**
O-6-120	**16.8**
N-6-79	**16.9**
N-6-80	**16.9**

N-6-81	**17.0**
N-6-82	**17.1**
N-6-83	**17.1**
O-6-121	**17.3**
O-6-122	**17.3**
N-6-84	**17.4**
N-6-85	**17.4**
N-6-86	**17.4**
N-6-87	**17.8**
N-6-88	**17.8**
N-6-89	**17.9**
N-6-90	**17.9**
N-6-91	**18.1**
N-6-92	**18.1**
N-6-93	**18.1**
N-6-94	**18.3**
N-6-95	**18.5**
N-6-96	**18.6**
N-6-97	**18.6**
N-6-98	**18.6**
N-6-99	**18.6**
N-6-100	**18.7**
N-6-101	**18.7**
N-6-102	**18.7**
N-6-103	**18.7**
N-6-104	**18.7**
N-6-105	**18.8**
N-6-106	**18.8**
N-6-107	**18.8**
N-6-108	**18.8**
N-6-109	**18.8**
N-6-110	**18.9**
N-6-111	**18.9**
N-6-112	**19.0**
N-6-113	**19.3**
N-6-114	**19.4**
N-6-115	**19.6**

N-6-116	**19.7**
N-6-117	**19.7**
N-6-118	**19.7**
N-6-119	**19.8**
N-6-120	**19.9**
N-6-121	**19.9**
N-6-122	**19.9**
N-6-123	**19.9**
N-6-124	**20.0**
N-6-125	**20.1**
N-6-126	**20.2**
N-6-127	**20.2**
N-6-128	**20.3**
N-6-129	**20.5**
N-6-130	**20.5**
N-6-131	**20.5**
N-6-132	**20.5**
N-6-133	**20.5**
N-6-134	**20.5**
N-6-135	**21.0**
N-6-136	**21.1**
N-6-137	**21.2**
N-6-138	**21.3**
N-6-139	**21.6**
N-6-140	**21.7**
N-6-141	**22.2**
N-6-142	**22.2**
N-6-143	**22.3**
N-6-144	**22.3**
N-6-145	**22.5**
N-6-146	**22.5**
N-6-147	**22.9**
N-6-148	**23.0**
N-6-149	**23.3**
N-6-150	**23.5**
N-6-151	**23.5**
N-6-152	**23.7**

N-6-153	**23.7**
N-6-154	**24.1**
N-6-155	**24.1**
N-6-156	**25.0**
N-6-157	**25.0**

Table S8 Gibbs free energy (80 K) of conformers of $PABAH^+(H_2O)_7$.

Conf.	**ΔG / kJ mol^{-1}**
O-7-1	**0.0**
O-7-2	**0.5**
O-7-3	**0.5**
O-7-4	**0.6**
O-7-5	**0.6**
O-7-6	**0.8**
O-7-7	**0.8**
O-7-8	**0.8**
N-7-1	**1.1**
N-7-2	**2.4**
O-7-9	**3.7**
N-7-3	**4.8**
O-7-10	**4.9**
O-7-11	**5.5**
O-7-12	**5.5**
O-7-13	**5.6**
O-7-14	**5.6**
O-7-15	**5.6**
O-7-16	**5.6**
O-7-17	**5.8**
N-7-4	**5.8**
O-7-18	**5.9**
O-7-19	**6.0**
O-7-20	**6.0**
O-7-21	**6.1**
O-7-22	**6.3**
O-7-23	**6.3**
N-7-5	**6.8**
O-7-24	**7.0**

N-7-6	**7.1**
N-7-7	**7.1**
O-7-25	**7.3**
O-7-26	**7.4**
O-7-27	**7.4**
O-7-28	**7.4**
O-7-29	**7.5**
O-7-30	**7.5**
O-7-31	**7.5**
O-7-32	**7.5**
N-7-8	**7.5**
N-7-9	**7.5**
N-7-10	**7.6**
O-7-33	**7.9**
O-7-34	**8.5**
N-7-11	**8.6**
N-7-12	**8.6**
O-7-35	**8.8**
O-7-36	**8.8**
O-7-37	**8.9**
O-7-38	**9.1**
O-7-39	**9.1**
O-7-40	**9.1**
O-7-41	**9.4**
O-7-42	**9.4**
O-7-43	**10.2**
O-7-44	**10.3**
N-7-13	**10.3**
O-7-45	**10.3**
O-7-46	**10.6**
O-7-47	**10.8**
O-7-48	**10.8**
O-7-49	**10.8**
O-7-50	**10.8**
O-7-51	**11.0**
O-7-52	**11.0**
N-7-14	**11.0**

O-7-53	**11.0**
O-7-54	**11.1**
O-7-55	**11.1**
O-7-56	**11.2**
O-7-57	**11.2**
O-7-58	**11.3**
O-7-59	**11.4**
O-7-60	**11.5**
O-7-61	**11.5**
O-7-62	**11.7**
O-7-63	**11.7**
O-7-64	**11.8**
O-7-65	**12.1**
O-7-66	**12.1**
O-7-67	**12.6**
N-7-15	**13.1**
O-7-68	**13.5**
O-7-69	**13.5**
O-7-70	**13.5**
O-7-71	**13.6**
N-7-16	**13.6**
N-7-17	**13.6**
O-7-72	**13.7**
O-7-73	**13.8**
N-7-18	**13.9**
O-7-74	**13.9**
O-7-75	**14.0**
O-7-76	**14.0**
O-7-77	**14.1**
O-7-78	**14.1**
O-7-79	**14.1**
O-7-80	**14.1**
O-7-81	**14.2**
O-7-82	**14.2**
O-7-83	**14.6**
O-7-84	**14.7**
O-7-85	**14.8**

O-7-86	**14.8**
O-7-87	**14.8**
N-7-19	**14.8**
O-7-88	**14.8**
N-7-20	**15.0**
O-7-89	**15.0**
O-7-90	**15.0**
O-7-91	**15.0**
O-7-92	**15.1**
O-7-93	**15.1**
O-7-94	**15.1**
O-7-95	**15.2**
O-7-96	**15.2**
O-7-97	**15.2**
O-7-98	**15.2**
O-7-99	**15.6**
O-7-100	**15.7**
O-7-101	**15.8**
O-7-102	**15.9**
O-7-103	**15.9**
O-7-104	**16.0**
O-7-105	**16.0**
O-7-106	**16.0**
O-7-107	**16.0**
O-7-108	**16.0**
O-7-109	**16.0**
O-7-110	**16.0**
O-7-111	**16.2**
N-7-21	**16.2**
O-7-112	**16.6**
N-7-22	**16.7**
N-7-23	**17.1**
O-7-113	**17.2**
O-7-114	**17.3**
O-7-115	**17.3**
N-7-24	**17.5**
O-7-116	**17.7**

O-7-117	**17.7**
O-7-118	**17.7**
N-7-25	**17.8**
O-7-119	**17.8**
O-7-120	**17.8**
O-7-121	**17.8**
N-7-26	**17.9**
N-7-27	**18.0**
N-7-28	**18.0**
N-7-29	**18.1**
N-7-30	**18.2**
N-7-31	**18.3**
N-7-32	**18.3**
N-7-33	**18.3**
O-7-122	**18.3**
N-7-34	**18.3**
O-7-123	**18.5**
N-7-35	**18.7**
N-7-36	**18.8**
O-7-124	**18.8**
O-7-125	**19.2**
N-7-37	**19.5**
N-7-38	**19.6**
N-7-39	**20.3**
N-7-40	**20.4**
N-7-41	**20.4**
N-7-42	**20.6**
N-7-43	**20.6**
O-7-126	**20.7**
N-7-44	**20.8**
N-7-45	**20.9**
N-7-46	**21.0**
N-7-47	**21.0**
N-7-48	**21.0**
N-7-49	**21.2**
N-7-50	**21.5**
N-7-51	**21.6**

N-7-52	**21.9**
N-7-53	**22.0**
N-7-54	**22.2**
N-7-55	**22.3**
N-7-56	**22.3**
N-7-57	**22.4**
N-7-58	**22.5**
N-7-59	**22.5**
N-7-60	**22.7**
N-7-61	**22.7**
N-7-62	**23.0**
N-7-63	**23.0**
N-7-64	**23.0**
N-7-65	**23.0**
N-7-66	**23.1**
N-7-67	**23.1**
N-7-68	**23.1**
N-7-69	**23.1**
N-7-70	**23.4**
N-7-71	**23.6**
N-7-72	**23.6**
N-7-73	**23.6**
N-7-74	**23.8**
N-7-75	**23.8**
N-7-76	**23.9**
N-7-77	**23.9**
N-7-78	**24.0**
N-7-79	**24.1**
N-7-80	**24.5**
N-7-81	**26.1**
N-7-82	**26.2**
N-7-83	**26.5**
N-7-84	**29.6**
N-7-85	**30.3**
N-7-86	**30.3**

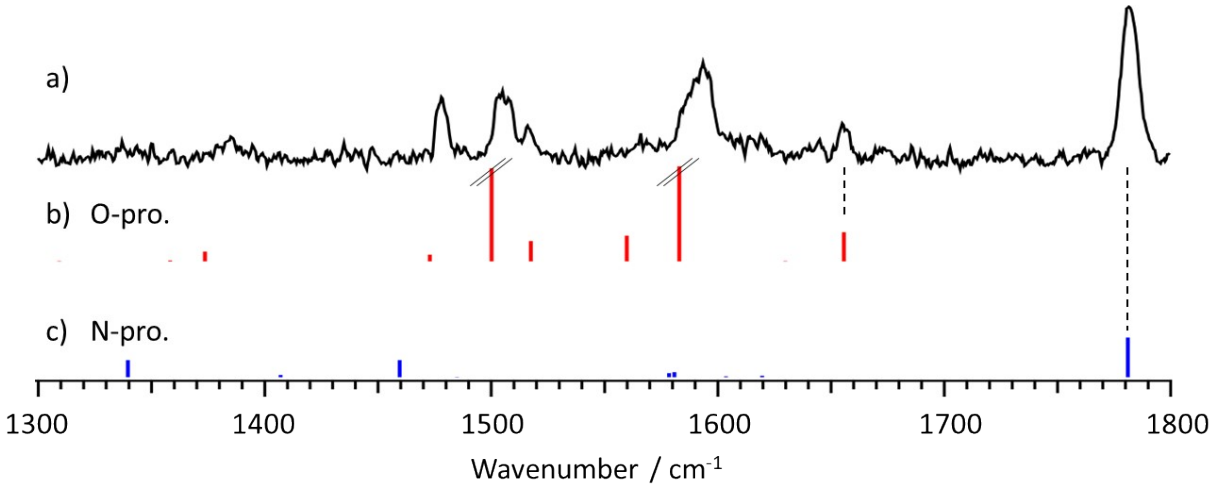

Fig. S1 a) IRPD spectra of $PABAH^+$ electrosprayed from an acetonitrile solution of PABA (10^{-5} M) with 0.5 % of formic acid. Consistent with the previous report,[1] the IRPD spectrum exhibits characteristic bands of both N- and O-protomers. Calculated IR spectra of the most stable b) O- and c) N-protomers of $PABAH^+$ are shown. The bands at 1655 and 1781 cm^{-1} are assigned to NH_2 bend of O-pro. and C=O stretch of N-pro., respectively. Scaling factors were determined as 0.970 (O-pro.) and 0.955 (N-pro.) using the characteristic bands.

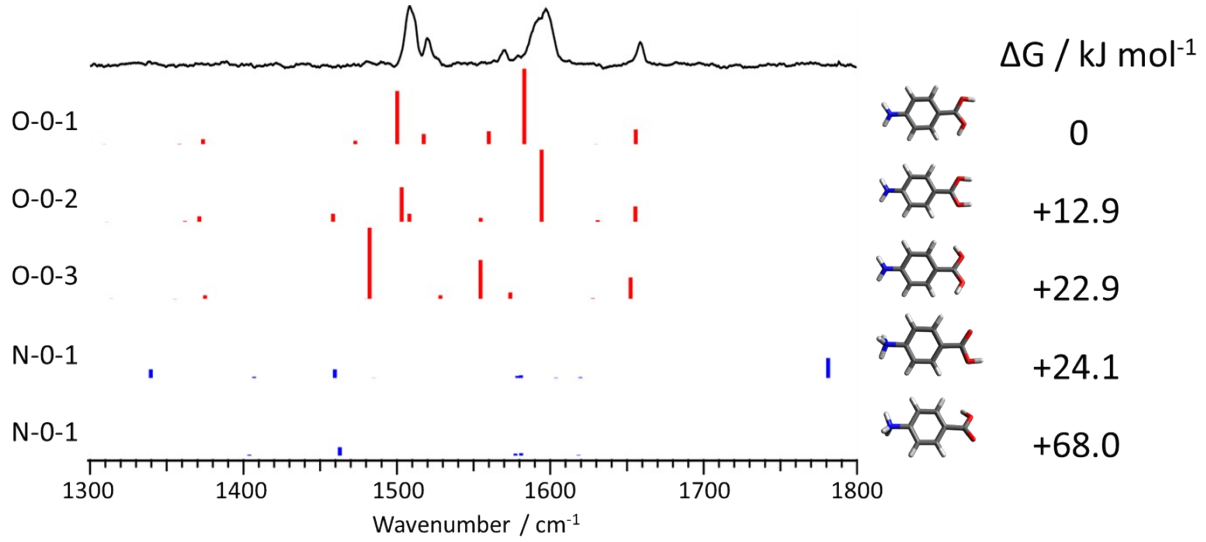

Fig. S2 Calculated IR spectra and structures of the five lowest energy conformers of $PABAH^+$ at 80 K. The bands at 1508, 1519, 1570, 1597, 1658cm^{-1} are reasonably reproduced by the calculated bands of O-0-1. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution so that only O-protomer appears.

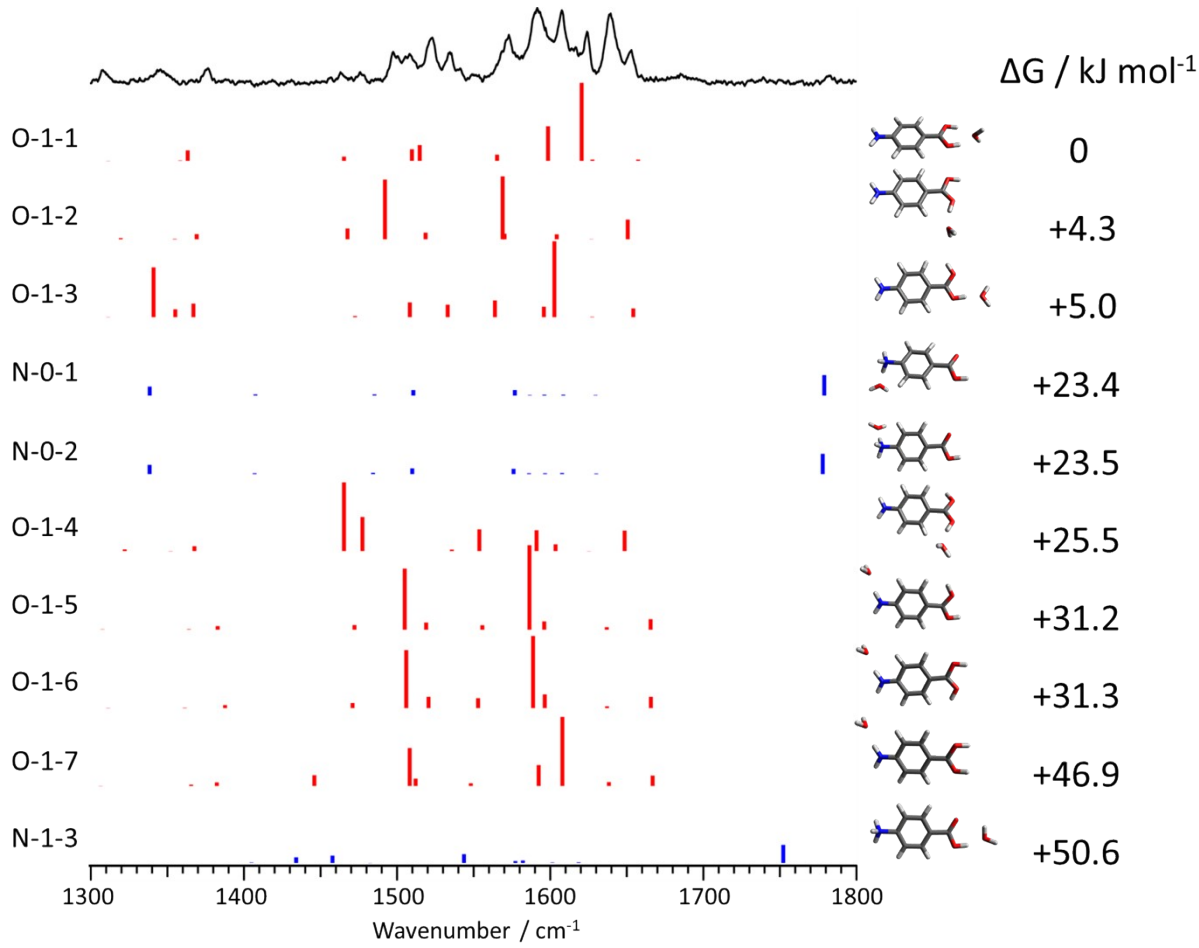

Fig. S3 Calculated IR spectra and structures of the ten lowest energy conformers of $PABAH^+$-$(H_2O)_1$ at 80 K. The bands in 1500-1700 cm^{-1} are reasonably reproduced by the calculated bands of O-1-1, O-1-2, and O-1-3. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

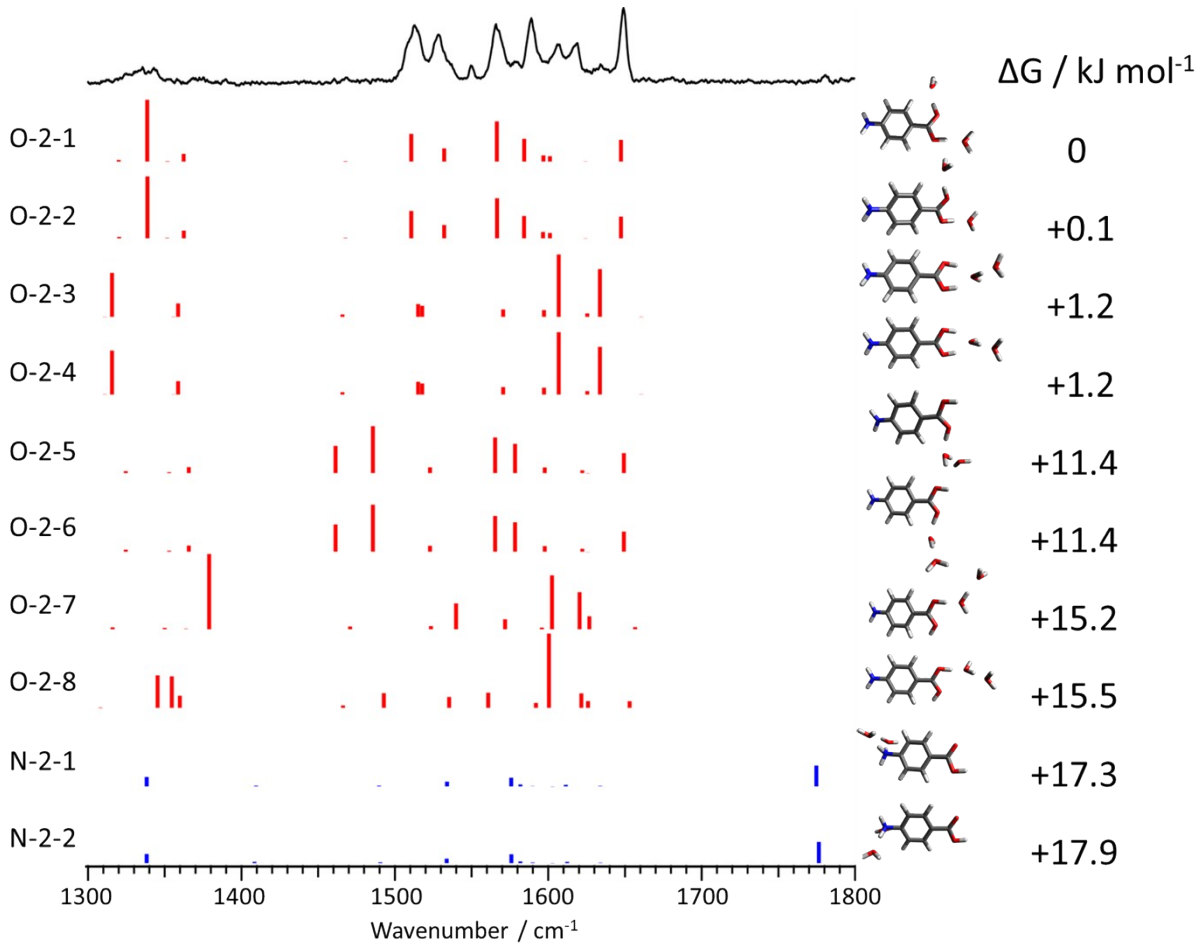

Fig. S4 Calculated IR spectra and structures of the ten lowest energy conformers of $PABAH^+$-$(H_2O)_2$ at 80 K. The bands in 1500-1700 cm^{-1} are reasonably reproduced by the calculated bands of O-2-1. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

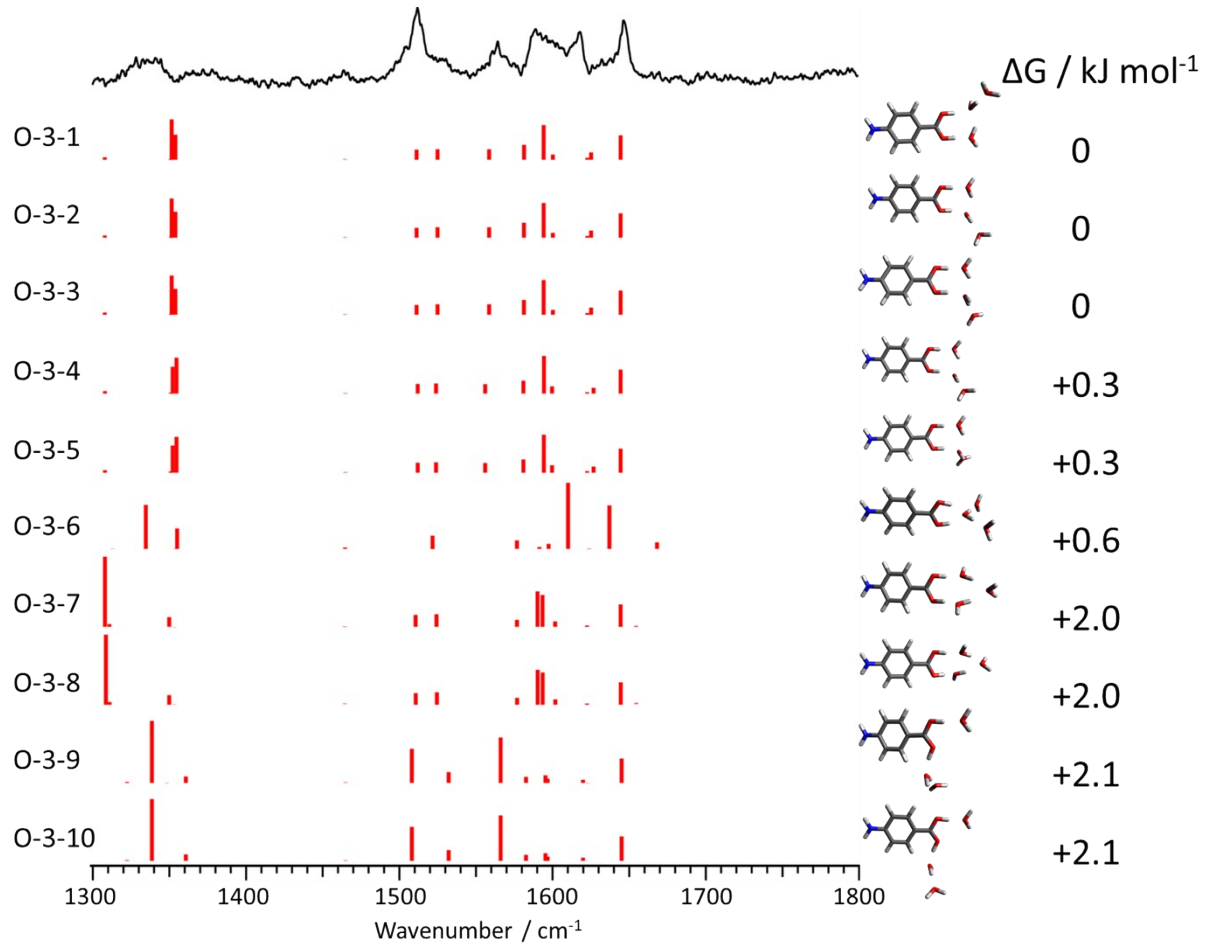

Fig. S5 Calculated IR spectra and structures of the ten lowest energy conformers of $PABAH^+$-$(H_2O)_3$ at 80 K. The bands in 1500-1700 cm^{-1} are reasonably reproduced by the calculated bands of O-3-1. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

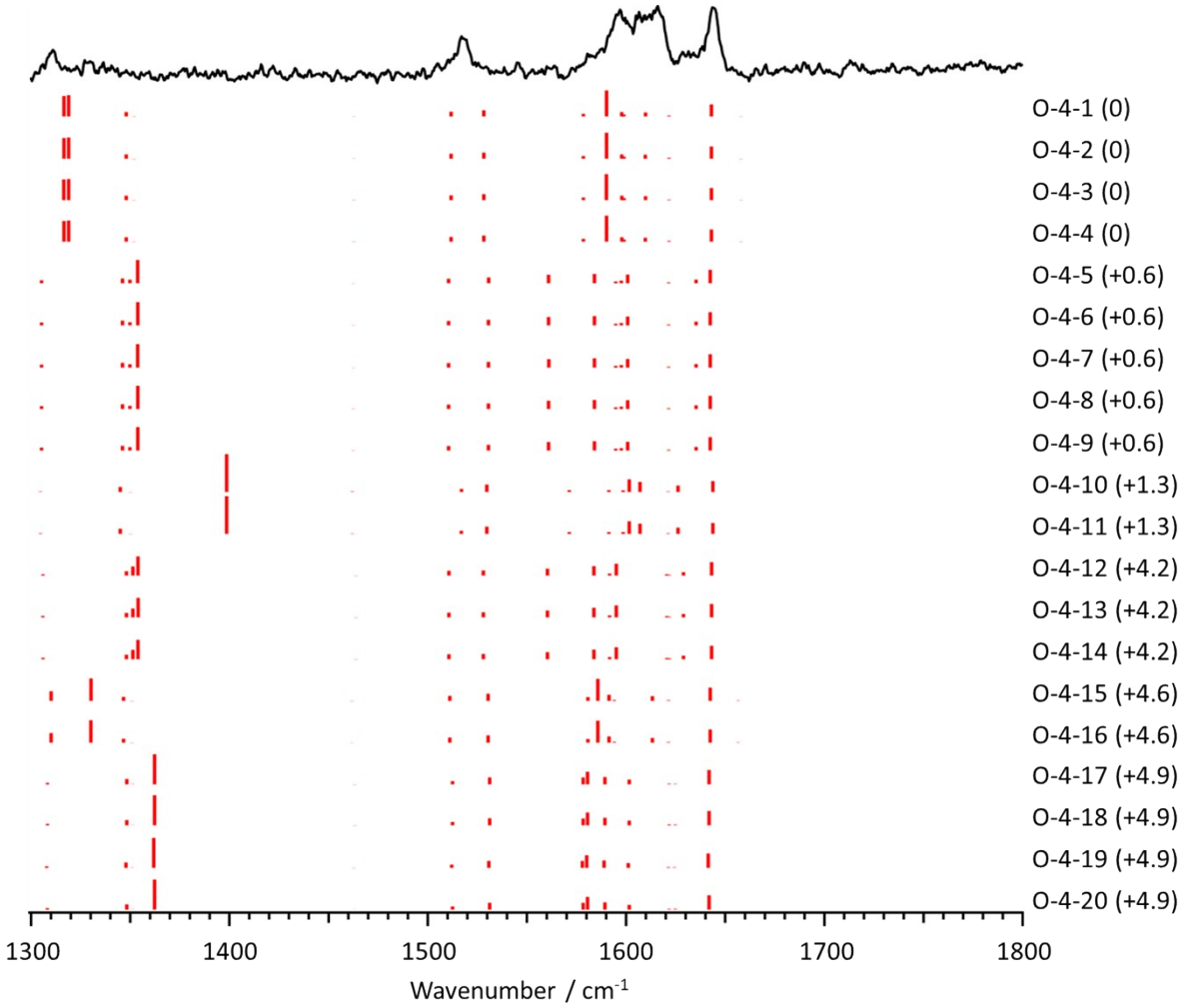

Fig. S6 Calculated IR spectra of the twenty lowest energy O-protomers of $PABAH^+$-$(H_2O)_4$ at 80 K. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

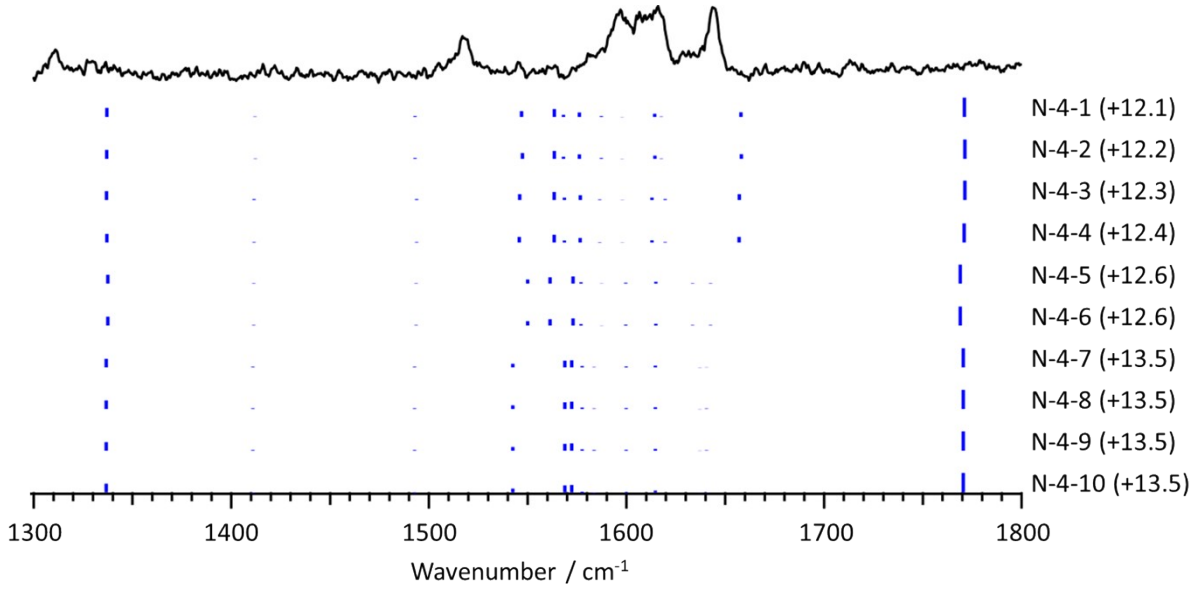

Fig. S7 Calculated IR spectra of the ten lowest energy N-protomers of $PABAH^+$-$(H_2O)_4$ at 80 K. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

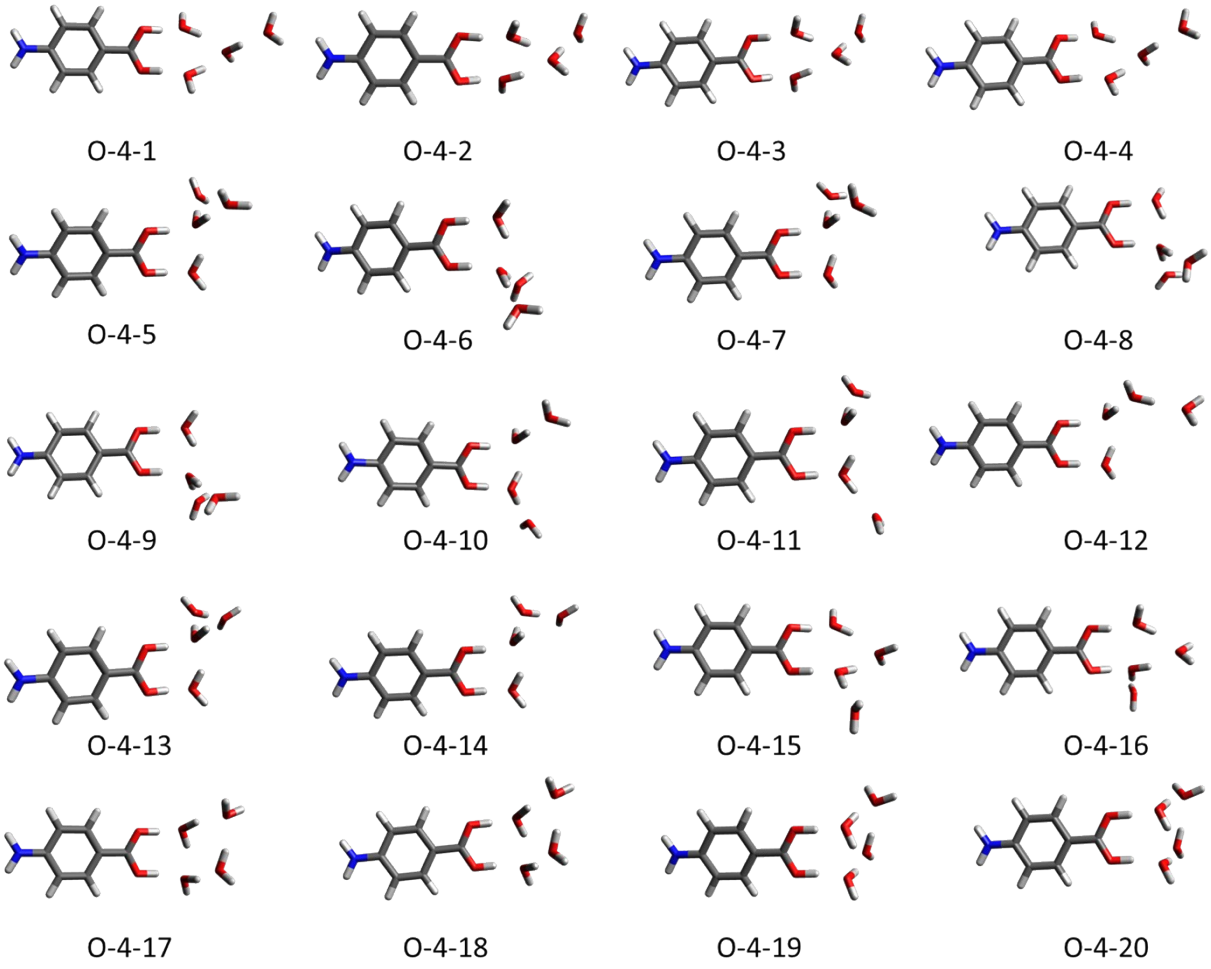

Fig. S8 Structures of the twenty lowest energy O-protomers of $PABAH^+$-$(H_2O)_4$ at 80 K.

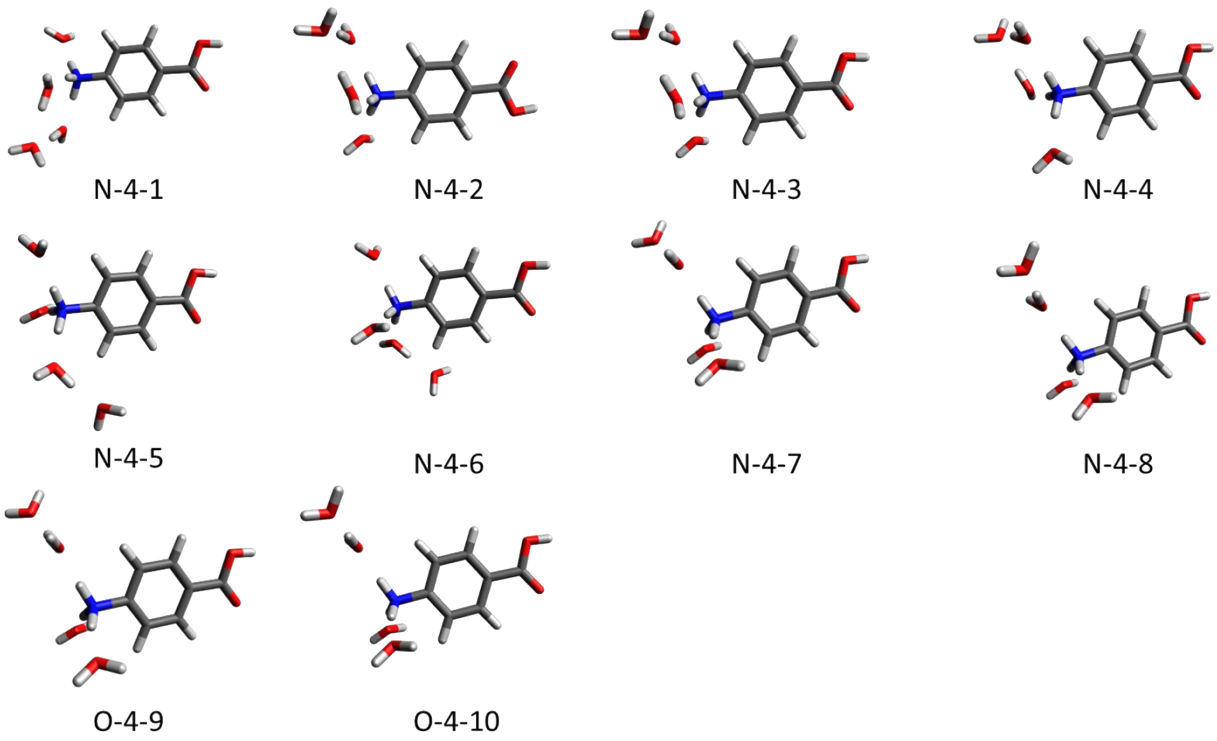

Fig. S9 Structures of the ten lowest energy N-protomers of $PABAH^{+}$-$(H_2O)_4$ at 80 K.

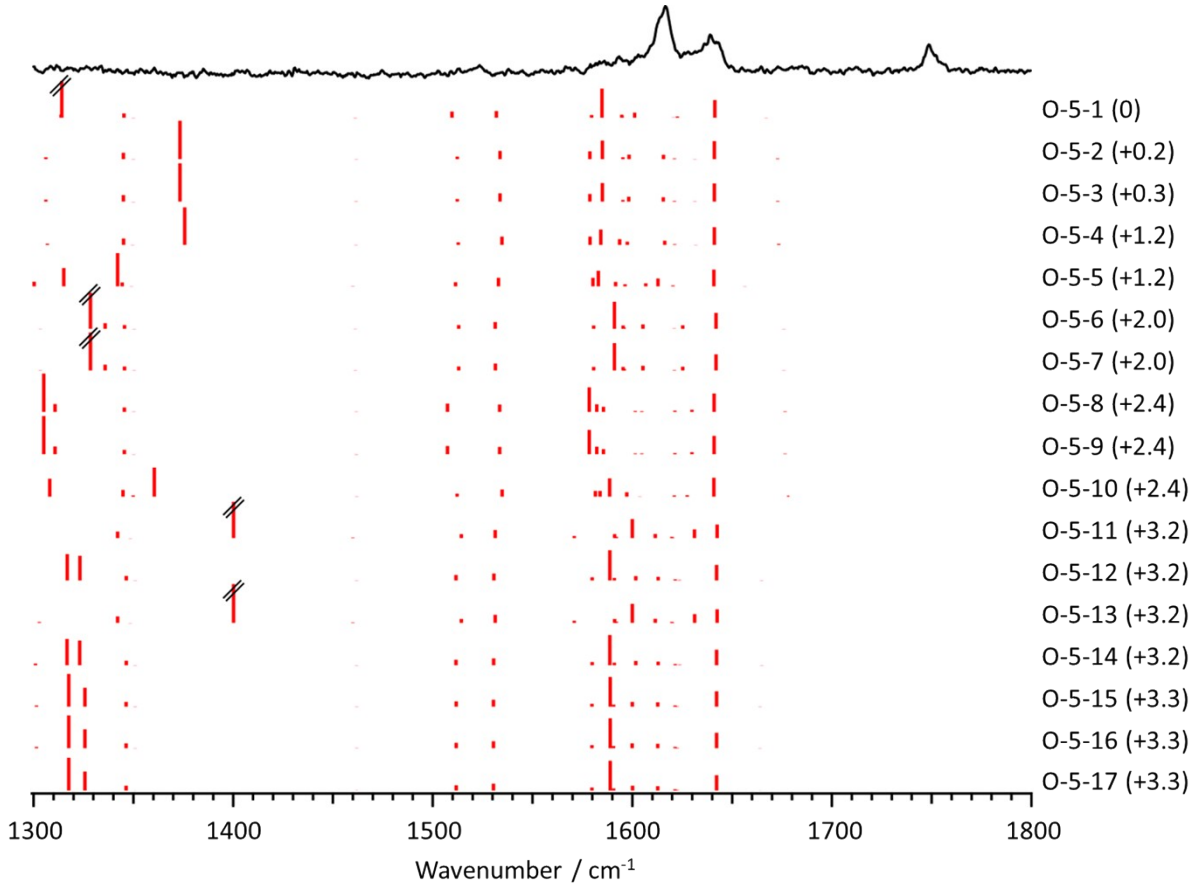

Fig. S10 Calculated IR spectra of the 33 lowest energy O-protomers(1-33) of $PABAH^+$-$(H_2O)_5$ at 80 K. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

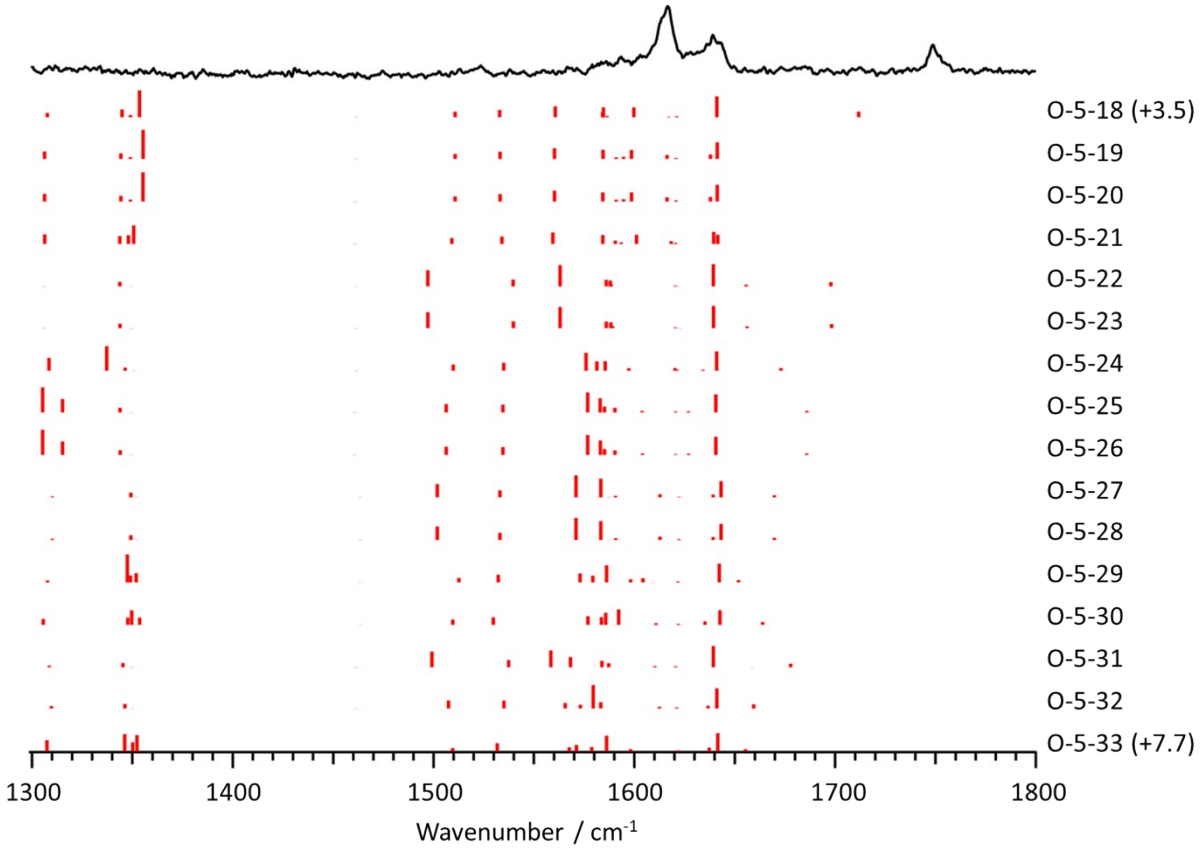

Fig. S10 Continued.

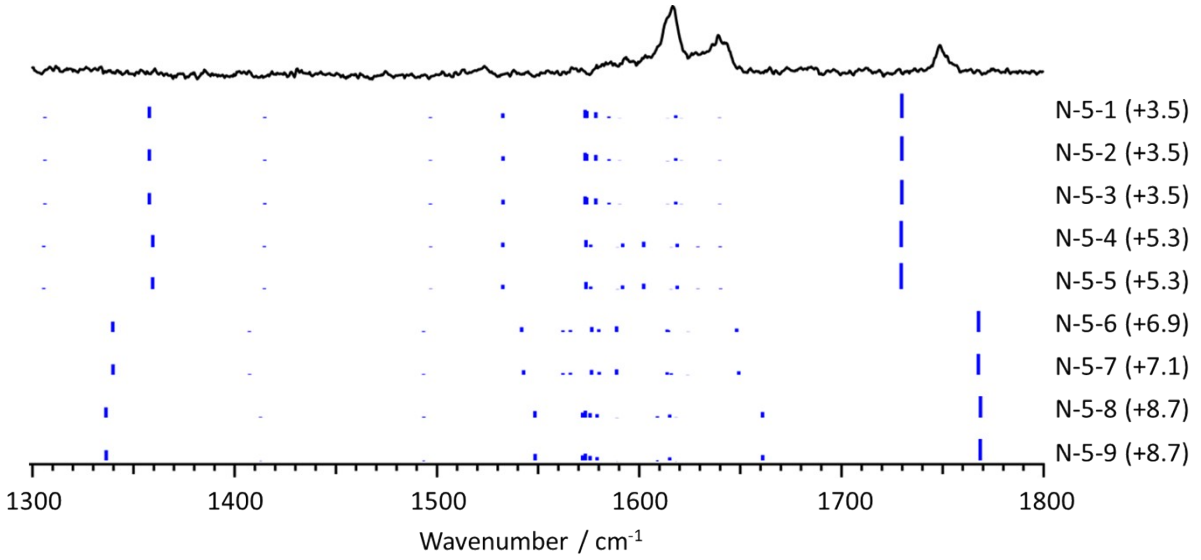

Fig. S11 Calculated IR spectra of the nine lowest energy N-protomers of $PABAH^+$-$(H_2O)_5$ at 80 K. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

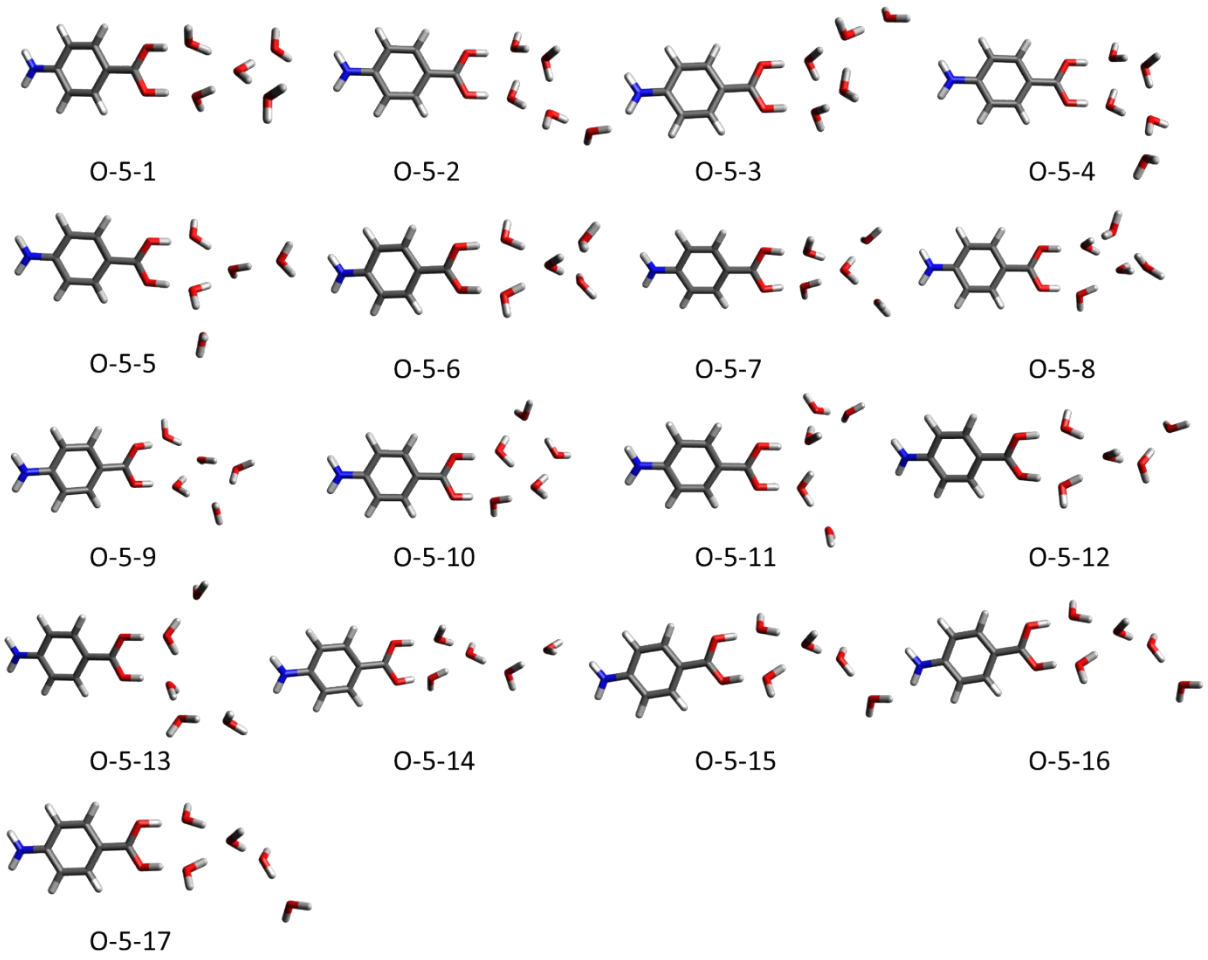

Fig. S12 Structures of the seventeen lowest energy O-protomers(1-17) of $PABAH^{+}$-$(H_2O)_5$ at 80 K.

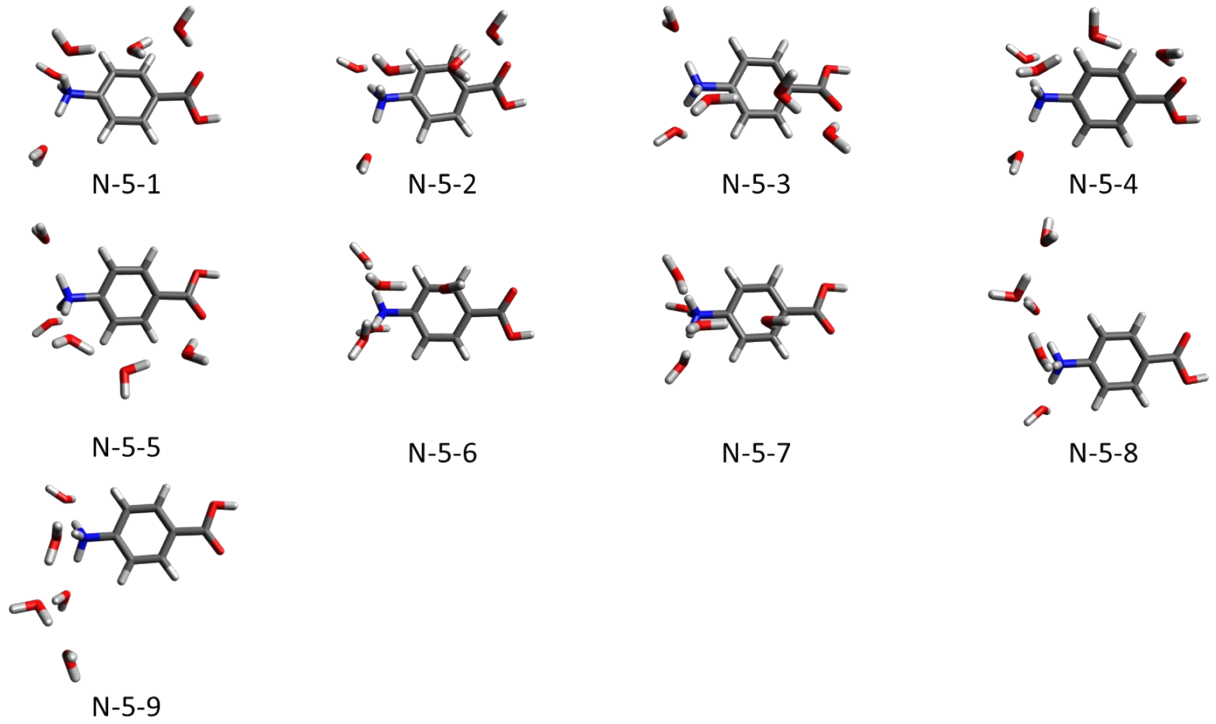

Fig. S13 Structures of the nine lowest energy N-protomers of $PABAH^{+}$-$(H_2O)_5$ at 80 K.

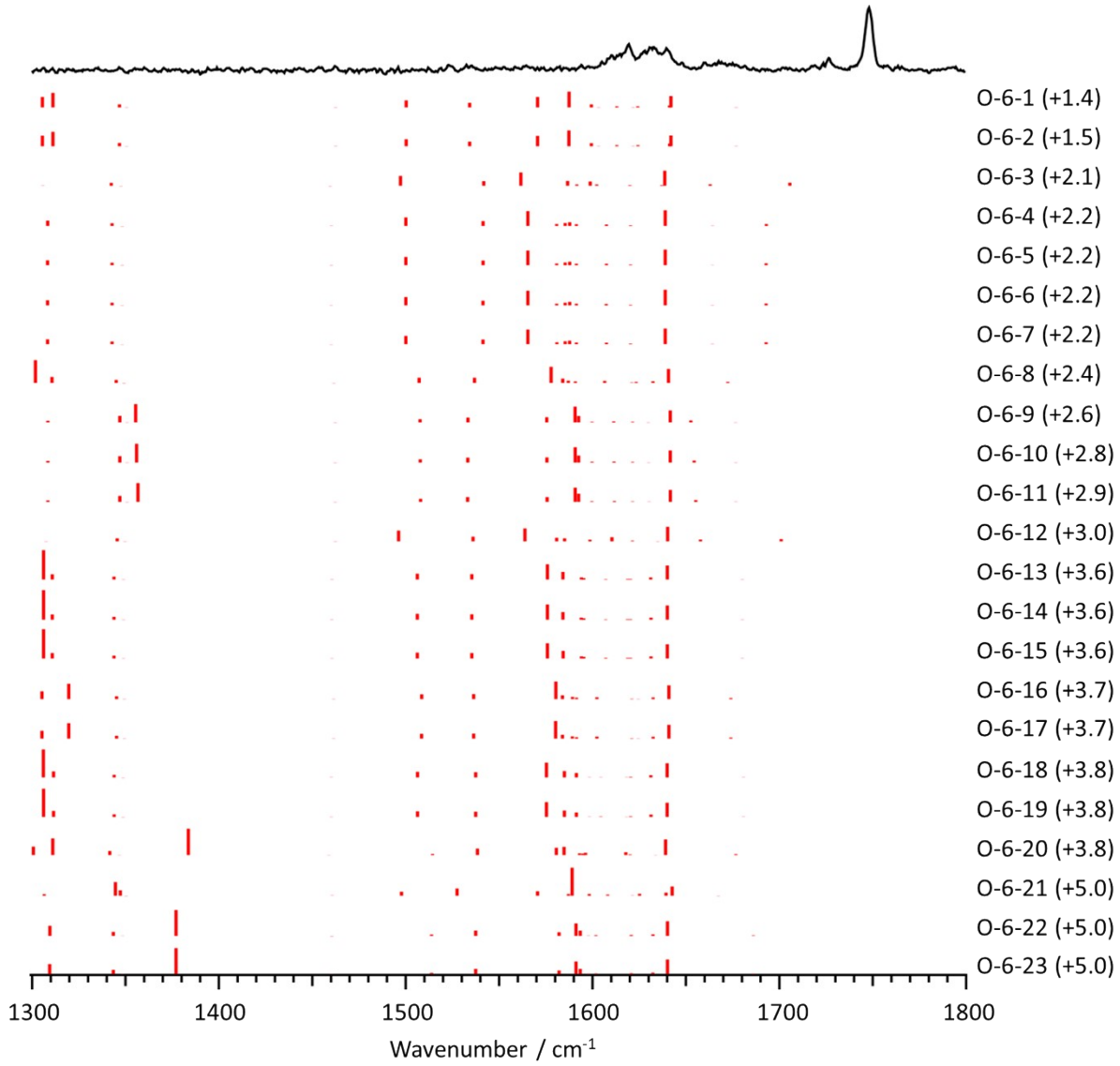

Fig. S14 Calculated IR spectra of the 46 lowest energy O-protomers(1-46) of $PABAH^+$-$(H_2O)_6$ at 80 K. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

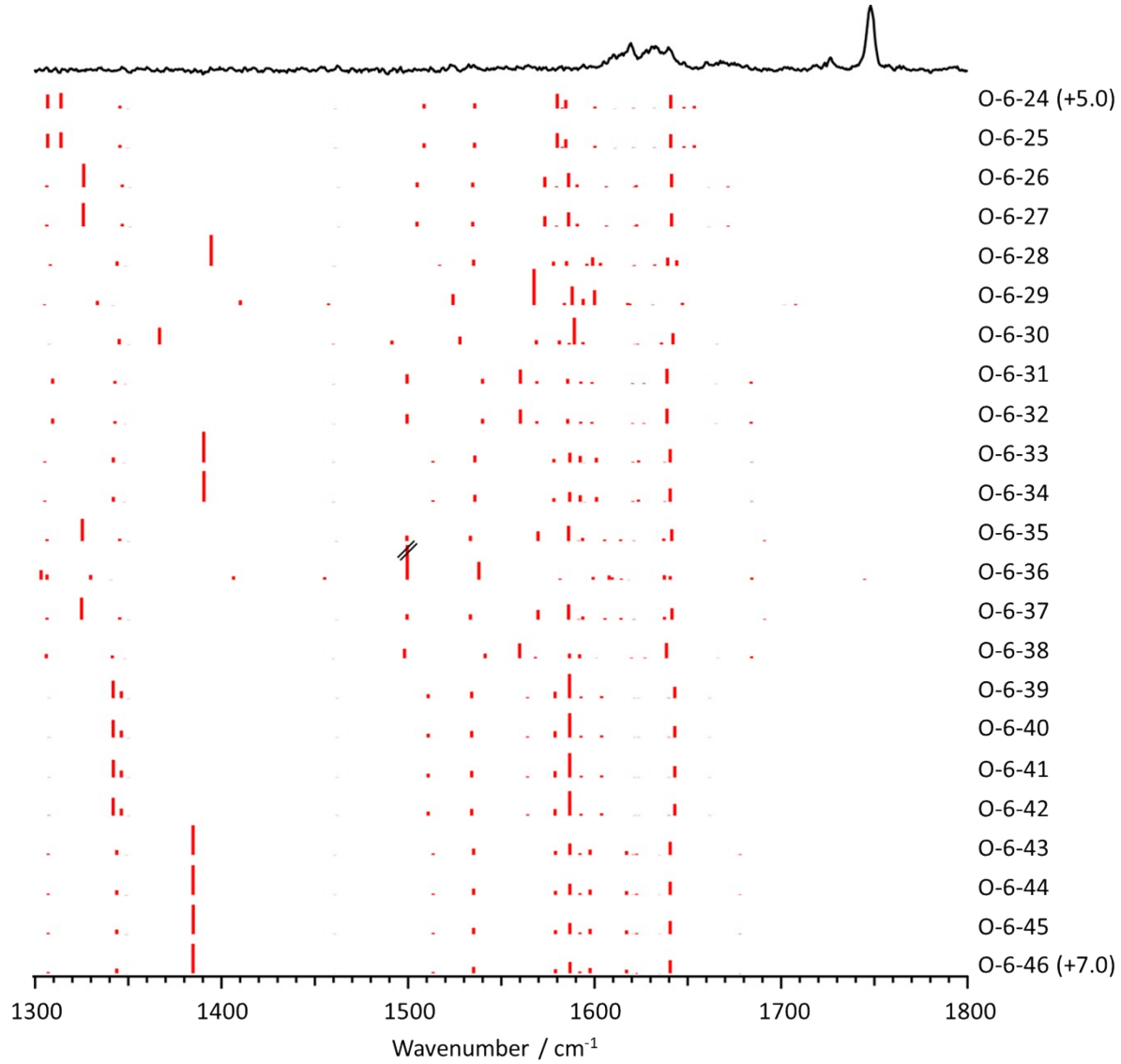

Fig. S14 Continued.

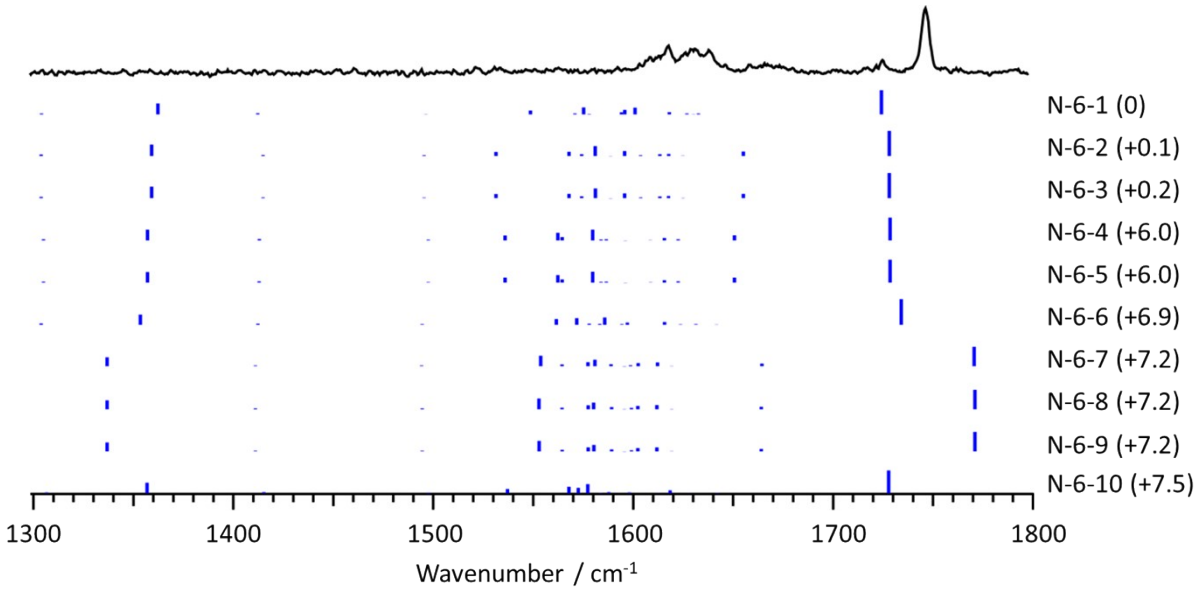

Fig. S15 Calculated IR spectra of the ten lowest energy N-protomers of $PABAH^+$-$(H_2O)_6$ at 80 K. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

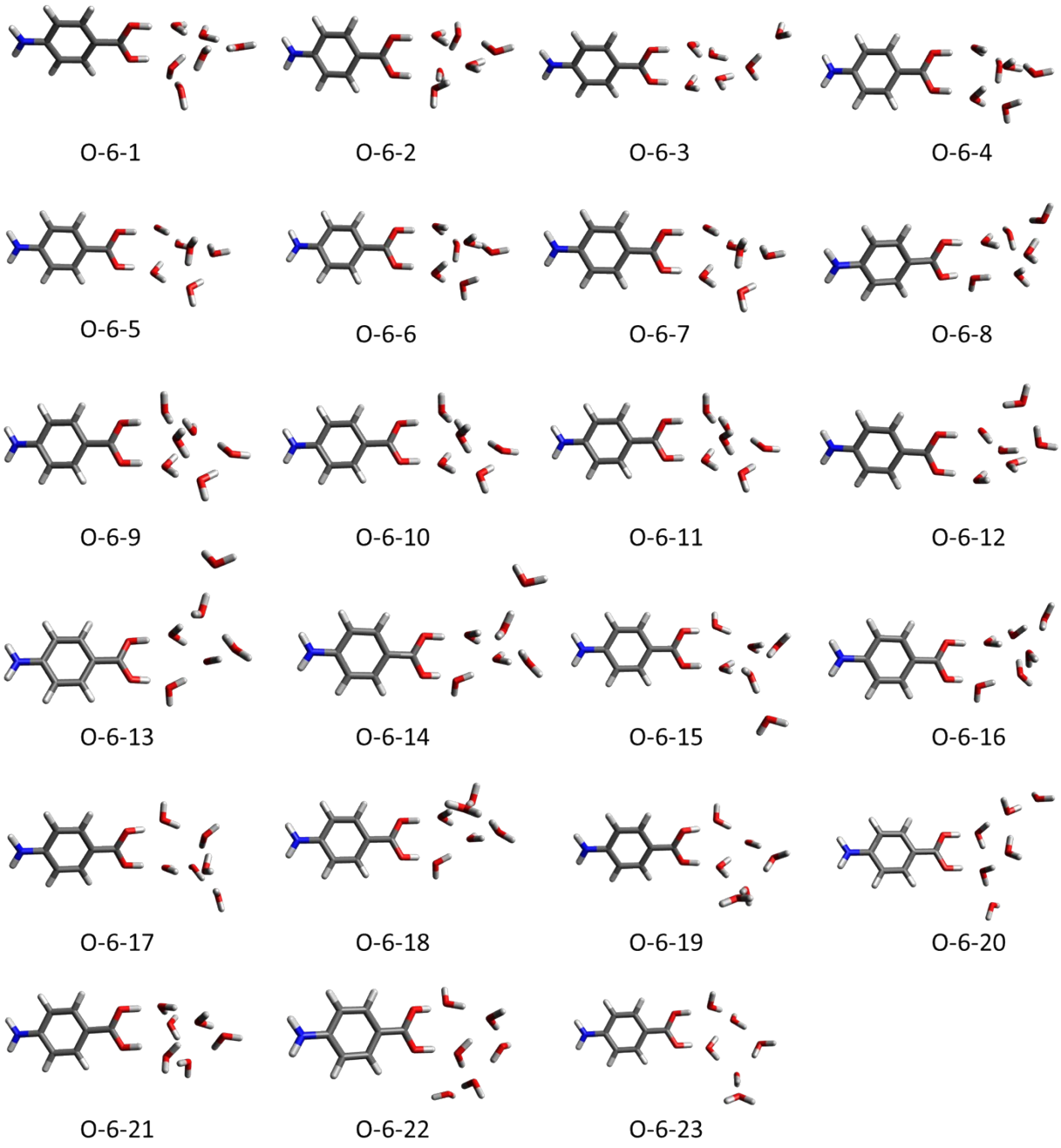

Fig. S16 Structures of the 23 lowest energy O-protomers(1-23) of $PABAH^{+}$-$(H_2O)_6$ at 80 K.

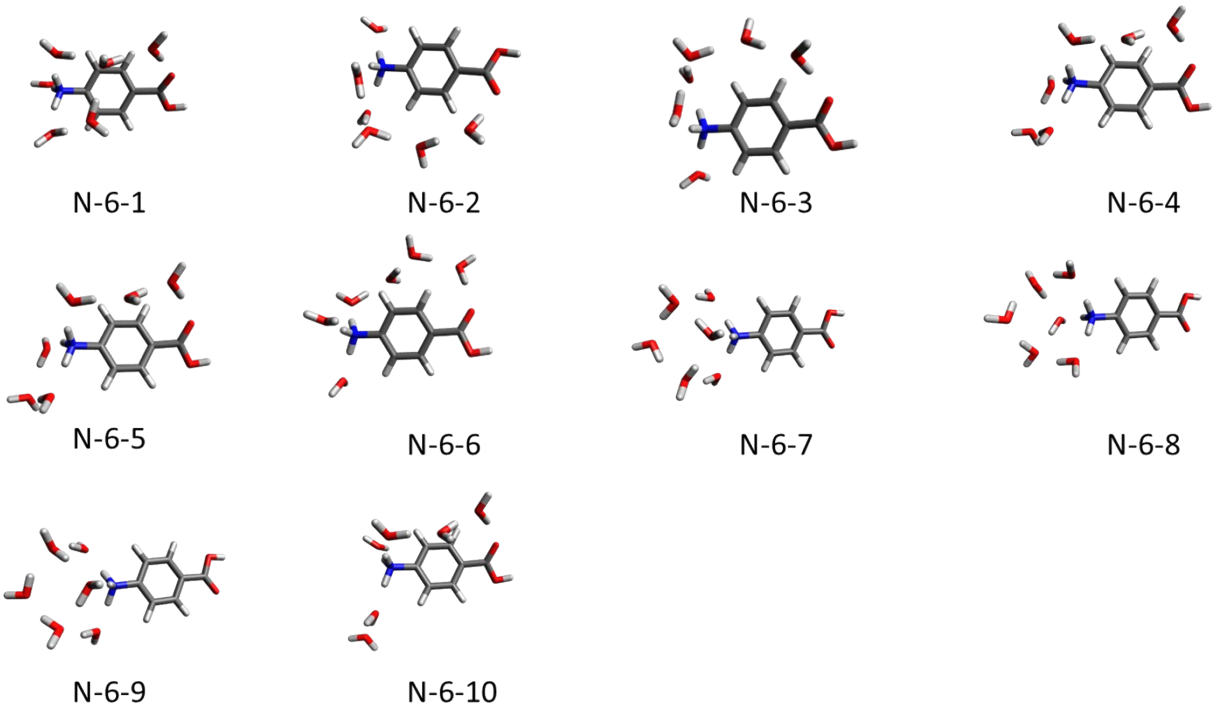

Fig. S17 Structures of the ten lowest energy N-protomers of $PABAH^+$-$(H_2O)_6$ at 80 K.

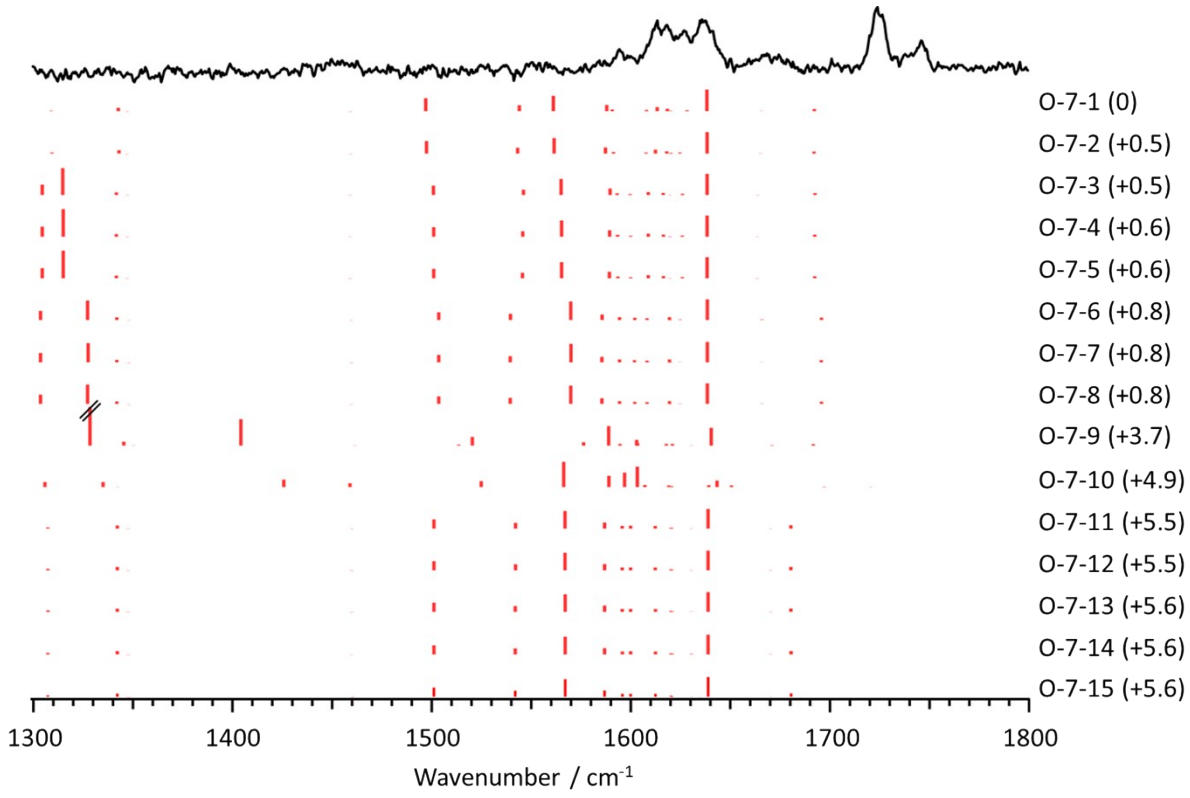

Fig. S18 Calculated IR spectra of the 15 lowest energy O-protomers of $PABAH^+$-$(H_2O)_7$ at 80 K. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

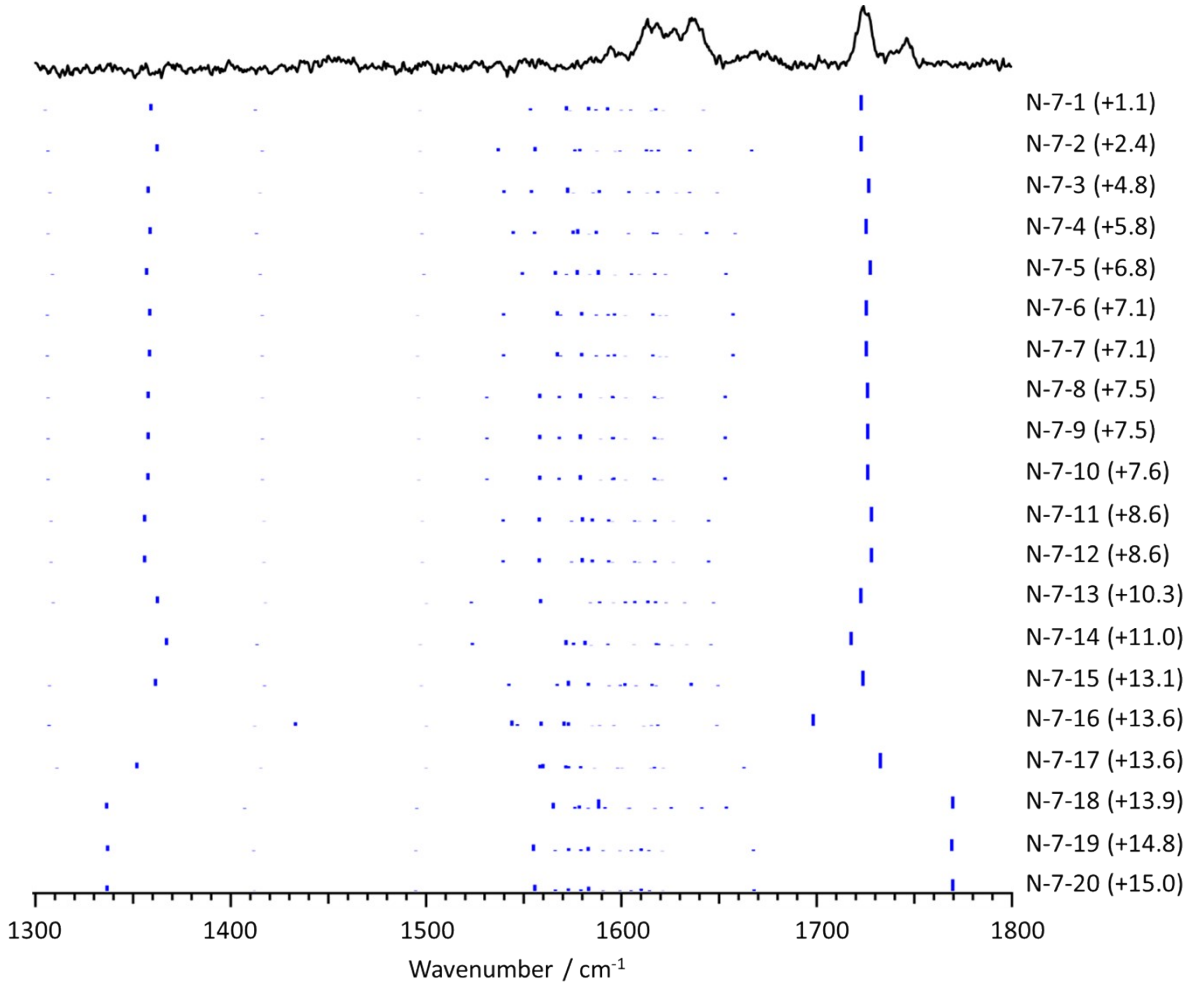

Fig. S19 Calculated IR spectra of the 20 lowest energy N-protomers of $PABAH^+$-$(H_2O)_7$ at 80 K. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

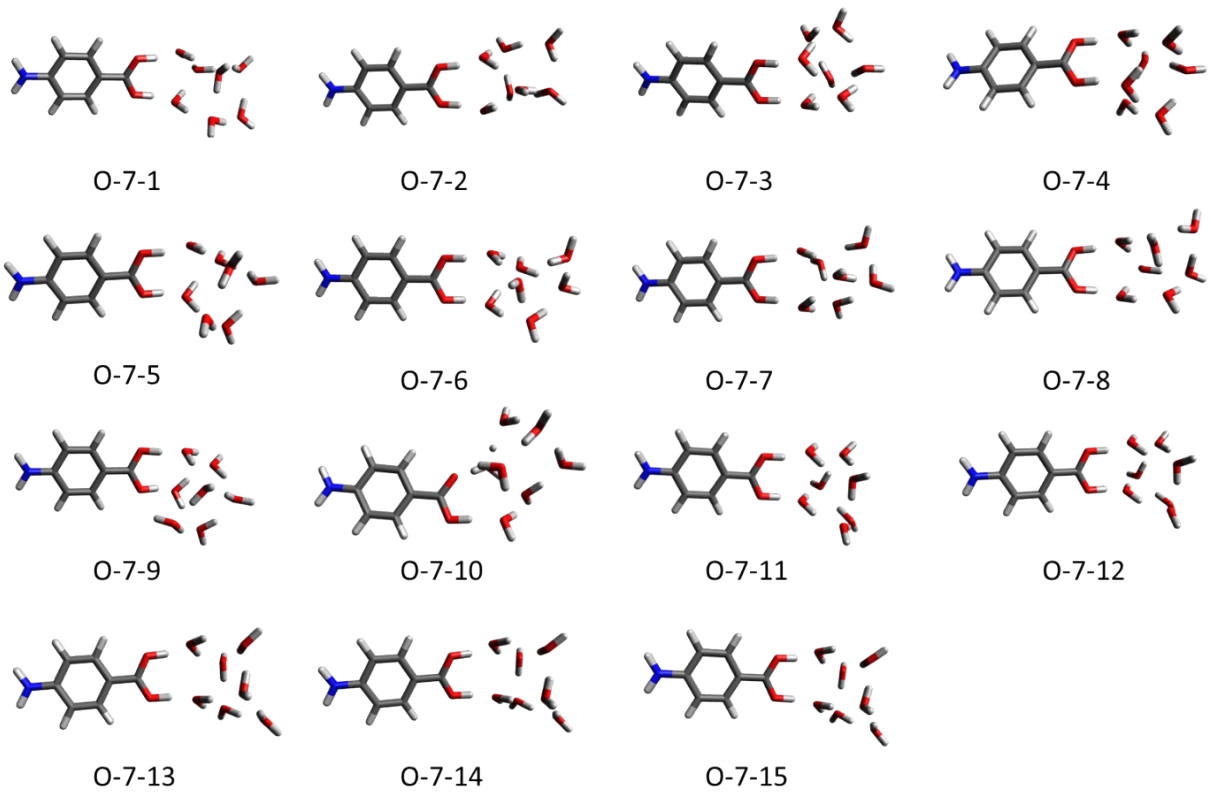

Fig. S20 Structures of the 15 lowest energy O-protomers of $PABAH^{+}$-$(H_2O)_7$ at 80 K.

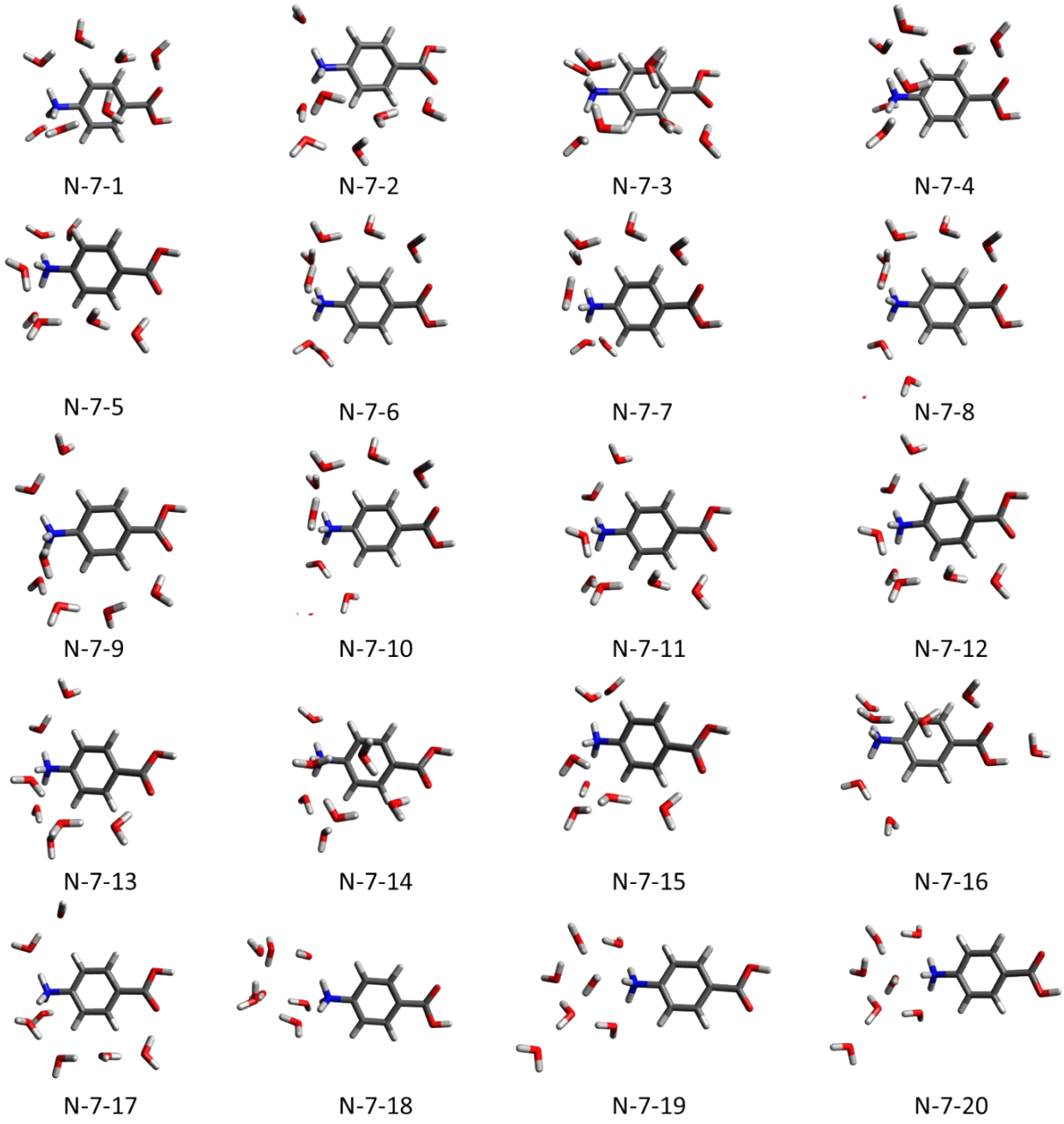

Fig. S21 Structures of the 20 lowest energy N-protomers of $PABAH^+$-$(H_2O)_7$ at 80 K.

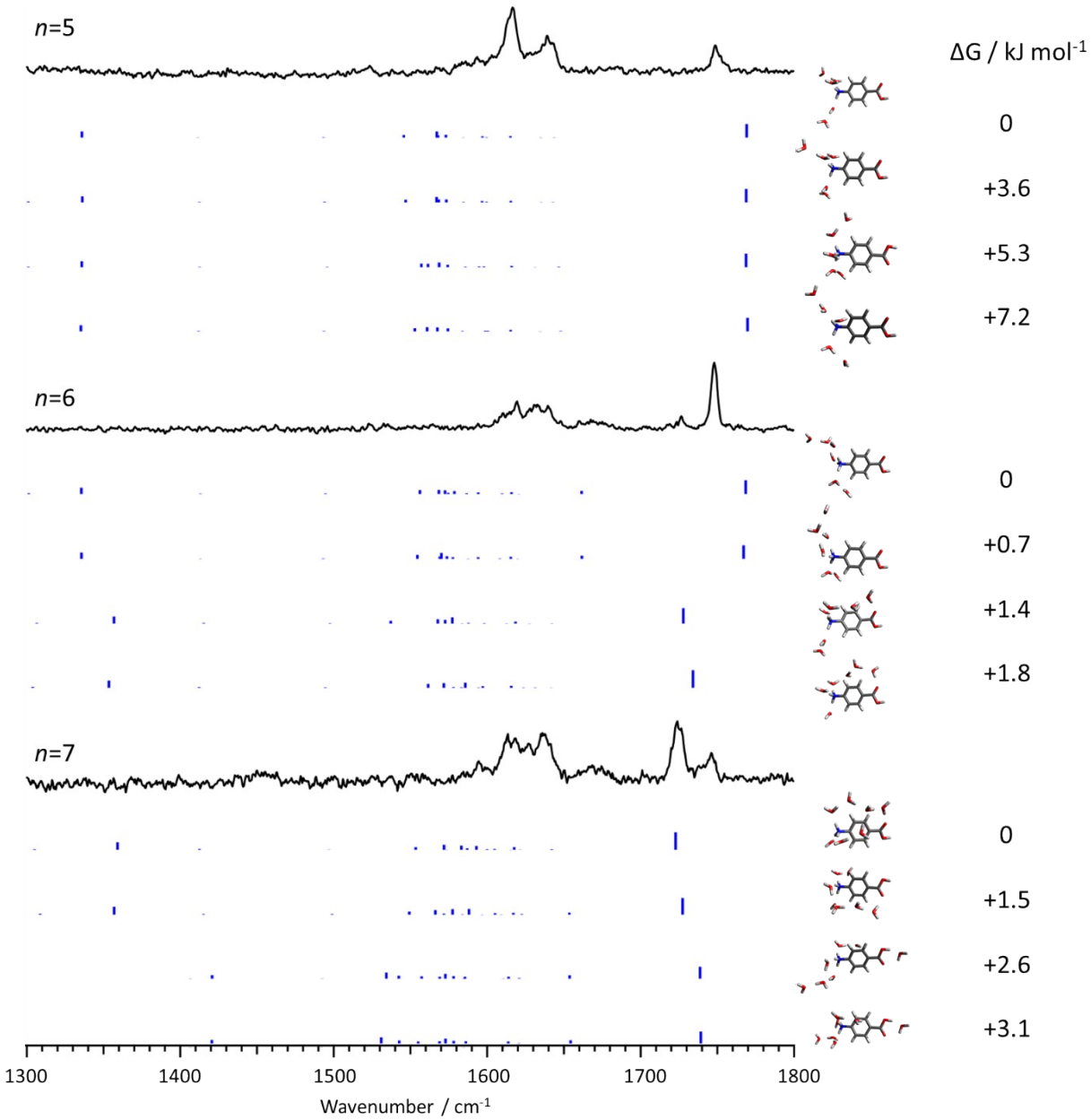

Fig. S22 Comparison of the IR spectra and energy of $PABAH^+$-$(H_2O)_n$ with N-protomer core at 298 K. Numbers indicated Gibbs free energy at 298 K. Observed spectrum shown at the top of the figure is measured from the electrospray from methanol solution.

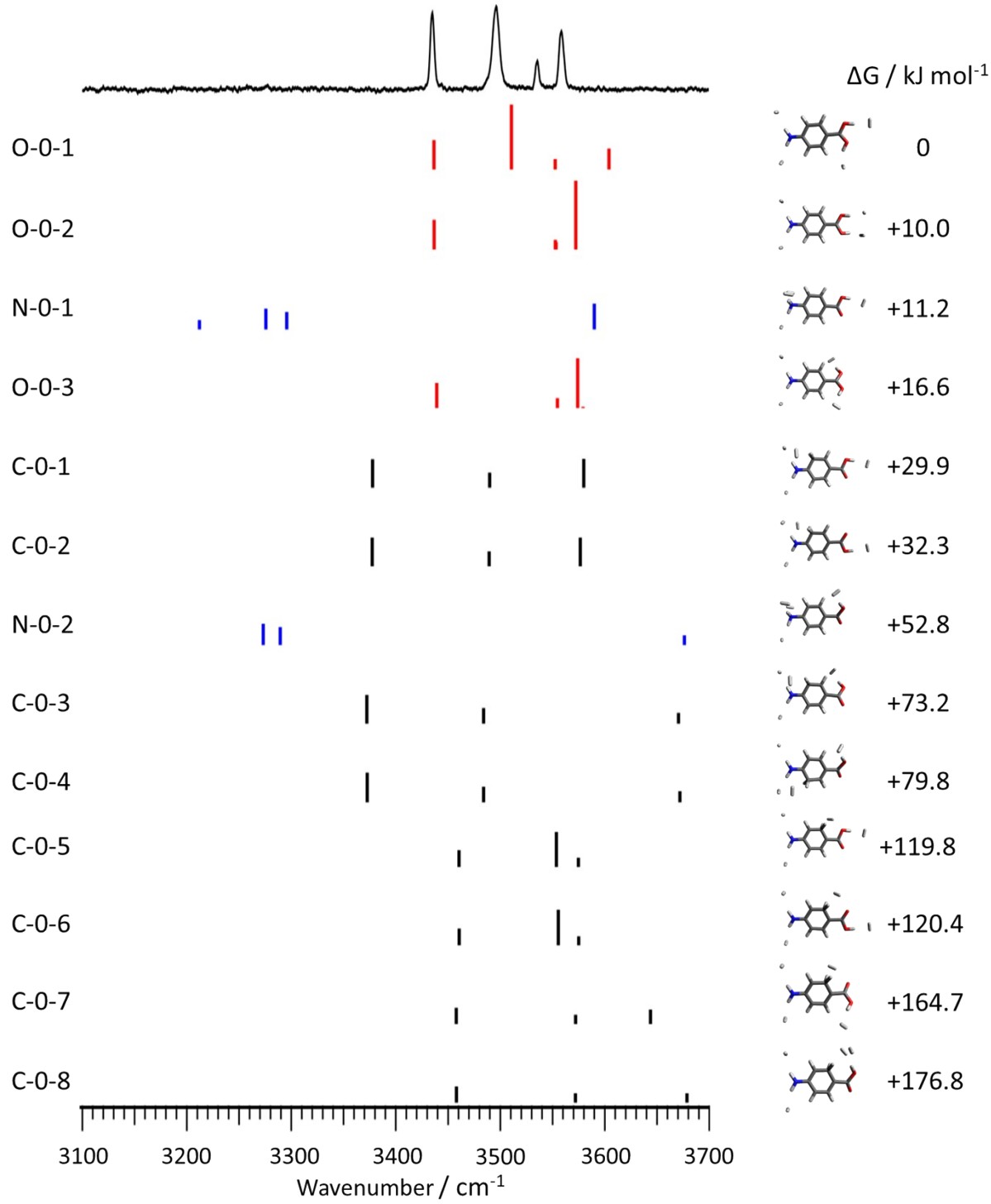

Fig. S23 Caluculated IR spectra of the ten lowest energy conformers of $PABAH^+(H_2)_4$. Numbers indicate Gibbs free energy at 298 K. In these calculations, C-protomer, whose proton is attaced on a carbon of the benzene ring, was calculated (from C-0-1 to C-0-8). C-protomer was found in protonated aniline,[2] but in the current IRPD spectrum, all the observed bands are assigned to those of O-protomer (O-0-1), neither to N- nor C-protomers.

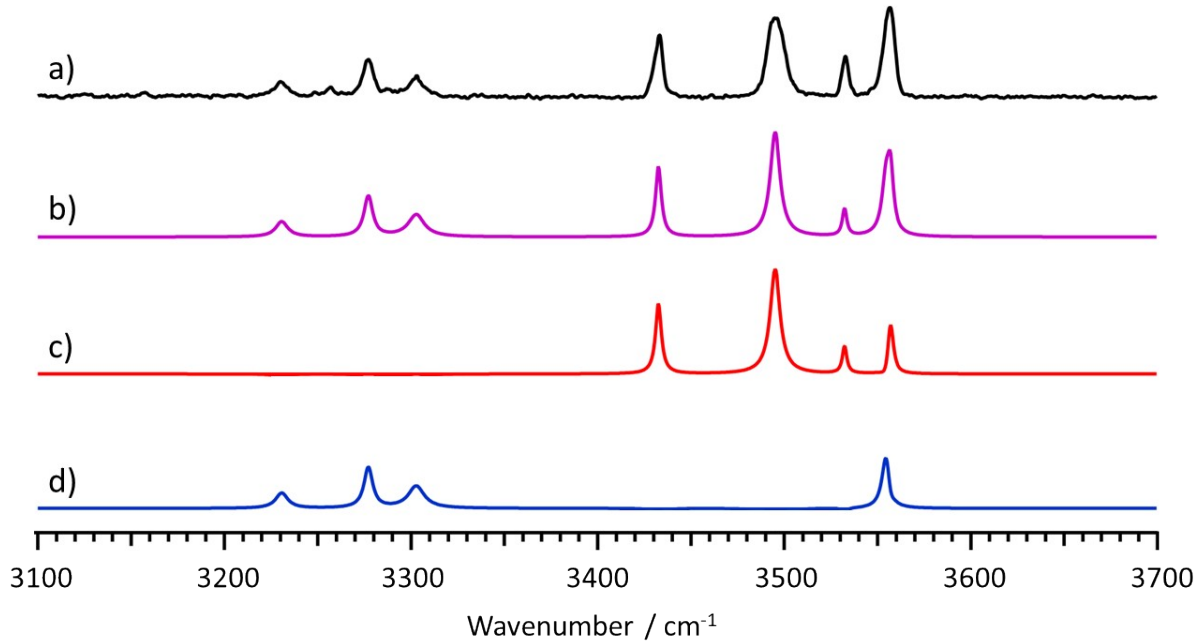

Fig. S24 a) CAS-IRPD spectrum of $PABAH^+(H_2O)_5$ and b) corresponding IR spectrum fitted by Lorentzian functions. The fitted spectrum is divided into c) O- and d) N-protomer IR spectra. First, the CAS-IR spectrum in a) was fitted with seven Lorentzian functions according to the seven experimental peaks. Four bands appear by subtracting the fitted curve of n=4 (only O-protomer exists) from the fitted curve for n=5. These four bands will stem from the N-protomer. By using these fitted bands as initial fitting parameters, the CAS-IR spectrum in a) was fitted again with eight Lorentzian functions (four bands for the N-protomer and four bands for the O-protomer) to obtain the spectrum in b). The standard deviations for the fitted intensities were within an error of 0.5-15% for individual bands. The errors for the derived averaged population ratios listed in Figure 5 are much smaller (<1%). The fitted curve b) was divided into the contributions from c) O-protomer and d) N-protomer by comparison with n=4 (only O-protomer exists). The relative protomer populations are then be estimated by normalizing the fitted band areas with calculated IR oscillator strengths. In this analysis, the population ratio was determined as the average of 16 estimated values (four bands for N-protomer × four bands for O-protomer).

References

1. T. Khuu, N. Yang and M. A. Johnson, *Int. J. Mass Spectrom.*, 2020, **457**, 116427.
2. Z. Karpas, Z. Berant and R. M. Stimac, *Struc. Chem.*, 1990, **1**, 201-204.